Commentary

TECHNOLOGY AND THE ACADEMICS

SIR ERIC ASHBY is always lively and in this ' Essay on Universities and the Scientific Revolution ' he says many things that are stimulating, many things which ' want saying ' as they express it in York-shire. In the first two chapters ' Science beyond the Channel ' and ' Science crosses the Channel ' he reviews the impact of scientific thinking on the universities of England on the one hand and of France and Germany on the other. Newton's heirs and successors were not, in England, academics and the sciences were regarded with suspicion. Quoting from the report of the Cambridge Univer-sity Commission of 1852: ' . . . Hitherto the study of chemistry has not only been neglected but discouraged in the University, as diverting the attention of pupils from what have been considered their proper academical studies '. And ' This ', as Ashby says, ' was evidence given a whole generation after Dalton had published his new system of chemical philosophy and after Berzelius had deter-mined the atomic weights of forty elements '[1]. It was otherwise in the Scottish universities.

There were three primary influences which brought a change; the professional impact of German research schools which had built on the success of the French; the alarm at the relative and rapid decay in British technical pre-eminence as evidenced by the dismal comparisons between the performances at the international exhibition in Paris in 1867 and the exhibition in London in 1851. The third lay in the extension and multiplica-tion of the various facets of the workers' education movement, a movement which had a considerable influence on the foundation of the new universities at the beginning of the century.

The survey is a preface, a background to the chapters ' Technology Adopted ' and ' Split Per-sonality in Universities '. In these the place of the technologies is examined. It is certainly true that the technologies are as yet tolerated, they are regarded in many senior common rooms with suffrance. This Ashby considers an error charged with grave consequences for the Universities. ' The habit of apprehending a technology in its complete-ness, this is the essence of technological humanism, and this is what we should expect education in higher technology to achieve. I believe it could be achieved by making specialist studies (whatever they are, metallurgy or dentistry or Norse philo-logy) the core around which are grouped liberal studies which are relevant to these specialist studies but they must be relevant; the path to culture should be through a man's specialism, not by by-passing it. Suppose a student decides to take up the study of brewing; his way to acquire general culture is not by diluting his brewing courses with popular lectures on architecture, social history and ethics but by making brewing the core of his studies. The *sine qua non* for a man who desires to be cul-tured is a deep and enduring enthusiasm to do one thing excellently. So there must first of all by an assurance that the student wants to make beer. From this it is a natural step to the study of biology, microbiology and chemistry; all subjects which can be studied not as techniques to be practised but as ideas to be understood . . .'

This is the kernel of Ashby's thesis. It is unfair to try to condense an essay of some hundred pages into less than a thousand words. Read the essay for yourself. It expresses a deep truth. Nevertheless as a practical thesis it requires careful examination. The intellectual compulsion required to carry a man through his specialism to the breadth and balance we seek is rare and outstanding. The problem is not how to educate the intellectual commandos. It is how to educate a new and much more numerous upper middle class in the specialisms which are necessary for material needs and indeed progress—for if the momentum dies, the society will wither—bearing in mind that most of candidates are not of the first rank. If the keys of the kingdom are simple principles, as they are, then brewing becomes a post-graduate study of microbiology. This is not of course the way to train people skilled in the art of brewing but it is the way to project the principles —and illuminate the principles of microbiology.

Learning and education are polarized activities at all levels from the cradle to the grave. If the educa-tion is not related to the victim's natural interest in his surroundings, his intellectual interest will not be roused; if it does not provide means of extending his experience beyond his immediate surroundings, it is not education which is learning by the experience of others. A man is educated when he has coordinated these two features for he is then in a position to learn. The purpose of a university training is surely to put a man into a position to learn.

[1] ASHBY, Sir ERIC *Technology and the Academics* London: Macmillan, 1958 (118pp., Price 15s)

B

SOME AUSTRALIAN RESEARCH ON WOOL

Part 1—Structure and Chemistry of Wool

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This article, the first of two parts, provides a brief but comprehensive review of the work that has been carried out over the past few years in the Melbourne laboratories of the Division of Protein Chemistry (formerly Biochemistry Unit), C.S.I.R.O., on the structure and chemistry of wool. The second article by Dr M. LIPSON, who is head of the Geelong laboratories, will deal with the processing of wool.

AUSTRALIAN wool textile research provides both for the immediate development of new and improved textile processes and for the accumulation of knowledge about the properties of wool to establish a sound basis of future processing developments. In 1949 the Commonwealth Scientific and Industrial Research Organization opened wool textile research laboratories for these purposes in Melbourne, Geelong and Sydney, and an outline is given here of some aspects of the research completed so far, mainly in the Melbourne laboratories, in the fields of wool structure and wool chemistry.

The programme adopted allows for close integration between investigations on the structure of wool at different levels of organization and also between these and investigations on wool processing. It also takes account of the origin of wool as a living tissue at the base of the wool follicle with all that this implies in terms of heterogeneity of histological structure and protein composition and sensitivity to changes in environment.

Wool Root and Associated Structures

Information about the wool fibre at its site of synthesis in the follicle has stemmed principally from the development of a wax sheet method of harvesting wool roots from sheepskins[1]. In outline, this method requires shearing the wool close to the skin surface, applying a molten beeswax–rosin mixture and, when cool, peeling the skin away from the wax sheet and cutting the roots projecting from the sheet with fine hair clippers (*Figure 1*). Aqueous extracts of wool roots prepared in this way contain the amino acids of wool in the free state although they are not all present in every preparation and uncombined cystine is rarely detected[2]. The total cystine content of the wool roots in fact is less than that of wool and almost all appears to be bound in high molecu-

lar weight peptides and proteins. Evidence of normal metabolic processes in the wool root cells is shown by the presence in the extracts of citric acid and other familiar chemical components of the tricarboxylic acid cycle and by the histological localization of the associated enzymes, succinic, α-glycerophosphoric, lactic and malic dehydrogenases[3]. Catalase, esterase, γ-glutamyl transpeptidase[4] and several phosphatases are also detected, a magnesium-activated pyrophosphatase being particularly active[5], and these enzymes might be expected to play an important role in the synthesis of wool proteins.

Wool roots may also provide more significant information on wool proteins than the fully hardened fibre since proteins can be extracted from this material by milder methods and the roots have already yielded fibrous elements resembling the microfibrils of the fibre[6].

A notable advance in hair and wool follicle biochemistry has been the isolation of a fibrous protein from the inner root sheaths of rat vibrissae containing at least six per cent of combined citrulline, little arginine and less than one per cent of cystine[7,8]. The presence of citrulline in wool follicle proteins has been demonstrated by analysis of the residues from urea-extracted wool roots and associated inner root sheaths. Citrulline has not previously been reported in protein combination and the presence of arginine but absence of citrulline in the inner root sheath at a lower level in the follicle suggests that the arginine may provide ammonia for enzymic amidation of the aspartic acid and glutamic acid residues in the growing wool fibre. Spaces visible between adjoining cells in Henle's layer of the inner root sheath could facilitate the flow of metabolites between the root and the surrounding capillary network[9].

Cortical Cells and Cuticle

The existence of bilateral structure in Merino wool fibres formed by deeply staining *ortho*-cortical cells on the outside of each crimp wave and poorly staining *para*-cortical cells on the inside has been amply confirmed. The *ortho*-cortex not only has

Figure 1. Harvesting wool roots for biochemical studies—the sheepskin has been peeled away towards the top of the picture leaving the wax sheet which holds the short fibres and exposes the roots for harvesting with the fine hair clippers

the greater affinity for dyestuffs but also swells more readily in alkali and is broken down preferentially into its constituent cells by trypsin acting under sterile conditions[10]. Treatment with peracetic acid reverses the selective affinity of the two segments for methylene blue, probably due to a higher content of cystine in the *para*-cortex and its oxidation to cysteic acid[11]. Examination of the roots of plucked fibres and of stained sections of skin cut through wool roots, shows that the bilateral structure of the fibre extends into the bulb[12,13]. In wools with little crimp, such as coarse Lincoln fibres and straight fibres from lustre mutant Merino sheep, no bilateral structure is visible. On the contrary the *ortho* cells are located centrally in the cortex and the *para* cells are nearer the cuticle[14].

Gold shadowing has allowed the optical microscope to be employed to the limit of its resolution in the study of wool structure[15]. Exocuticle for example is shown to be attached to epicuticle in the membrane enclosing the bubbles formed on the surface of wool fibres in the bromine Allworden reaction[16]. It reveals surface damage to the fibres by trypsin, bromine water or chlorine[17], fusion together of the scale cells of wool along the lines of contact to form a continuous epicuticle[18] and, in conjunction with phase contrast microscopy, gold shadowing shows clearly the structural features of the peracetic acid residues from wool, including

cortical cell membranes, nuclear membranes and remnants, and associated resistant fibrils[19].

Fibrils, Microfibrils and Proteins in the Intact Fibre

The use of thin sectioning techniques in conjunction with synthetic resins as embedding media[20] has enabled rapid advances to be made in the electron microscopy of wool fibres (see *Figure 2*). In sections of sheepskin stained with osmic acid, fibrils are seen inside the cortical cells of the wool root separated by regions of much lower density and, within the fibrils, microfibrils about 70Å in diameter arranged in sheets, in quasi-hexagonal patterns and in whorls[21] (see *Figure 3*). In the fully keratinized fibre the fibrils are packed together much more closely than in the root although, in the *ortho* segment, amorphous protein visible between the fibrils could provide access for reagents affecting this segment[22].

Individual microfibrils are visible within the fibrils after oxidation with peracetic acid and extraction

Figure 2. Cutting thin sections of wool fibres for electron microscopy—Araldite has been found suitable as an embedding medium for tough structures such as wool fibres

with neutral buffer solution to remove the matrix protein. This extracted protein contains more than twice the concentration of cystine found in the parent wool. Both the endocuticle and exocuticle are derived from granular structures and, unlike the cortex, they reveal no fibrous elements.

A new interpretation of the low angle x-ray diffraction pattern of wool has enabled the microfibrilla structure, as revealed by the electron

microscope, to be reconciled[23],[24] with the equatorial reflections of 86, 45 and 28Å. (An x-ray diffraction equipment as used in studying wool fibres is shown in *Figure 4*.) This interpretation is assisted by the

Figure 3. Electron micrograph of part of a cross-section of a wool fibre packed with microfibrils about 60Å in diameter and darker matrix. This structure is revealed in the intact fibre if the wool is reduced with thioglycollate before staining with osmic acid. Portions of several cortical cells are shown separated by intercellular cement (reduced to two-thirds of original size by reproduction)

observation that these reflections are intensified by reaction with osmic acid and also by reaction with lead and mercury salts following reduction[25]. In addition to the well known broad equatorial reflection corresponding to the 9·8Å spacing, a weak reflection of 16·8Å is intensified by treatment with mercuric acetate or by reduction and treatment with lead acetate, suggesting the presence of groups of α-helices in the microfibrils (see *Figure 5*). Certain meridional reflections, corresponding to repeats of pattern in the direction of the fibre axis, are also sharpened and slightly intensified by treatment with mercuric acetate solution. The action of iodine, in ethanol solution, shows other effects on the meridian pointing to the presence of tyrosine residues in the crystalline regions.

Certain features of the x-ray diagram of wool are accounted for by compound helical structures, but the mean molecular volume of the individual amino

acids calculated from these models[3] exceeds 140Å, the value calculated from the mean molecular weight of 111 based on an analysis of porcupine quill tip and the observed density[26],[27]. A further deficiency in the helical structure proposed for proteins is its failure to accommodate intra-chain disulphide bonds and proline, both of which are believed to be important constituents of keratinous proteins. Model building has shown that both needs are satisfied if the helix reverses direction where these amino acids occur in the peptide chain[28].

Measurement of the infra-red absorption spectra of wool fibres in the 2μ region has provided information about the orientation, configuration and accessibility of wool[29],[30]. The orientation of the side chain amide groups in wool, determined from the absorption in this region by well dried specimens, is such as to facilitate hydrogen bonding between adjacent polypeptide chains[31-32-33]. When dry wool is treated with deuterium oxide the amide group absorption is eliminated and this is interpreted as showing either that all these groups are concentrated in the non-crystalline region of the fibre or that the side chains in the crystalline region are accessible to water. The latter alternative is supported by x-ray diffraction evidence showing that the crystallites expand on hydration. About 30 per cent of the peptide hydrogen atoms are not replaced by deuterium and these are assumed to be in the crystalline microfibrils.
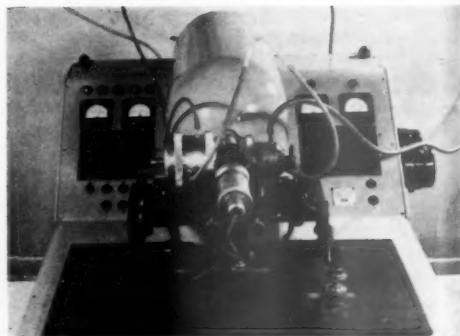

Figure 4. An x-ray diffraction equipment showing the microfocus camera used in studying wool fibres and similar keratinous structures

Proteins Extracted from Wool

While detailed information about the chemical structure and properties of individual wool proteins cannot be derived from examination of the intact fibre, many informative procedures are applicable
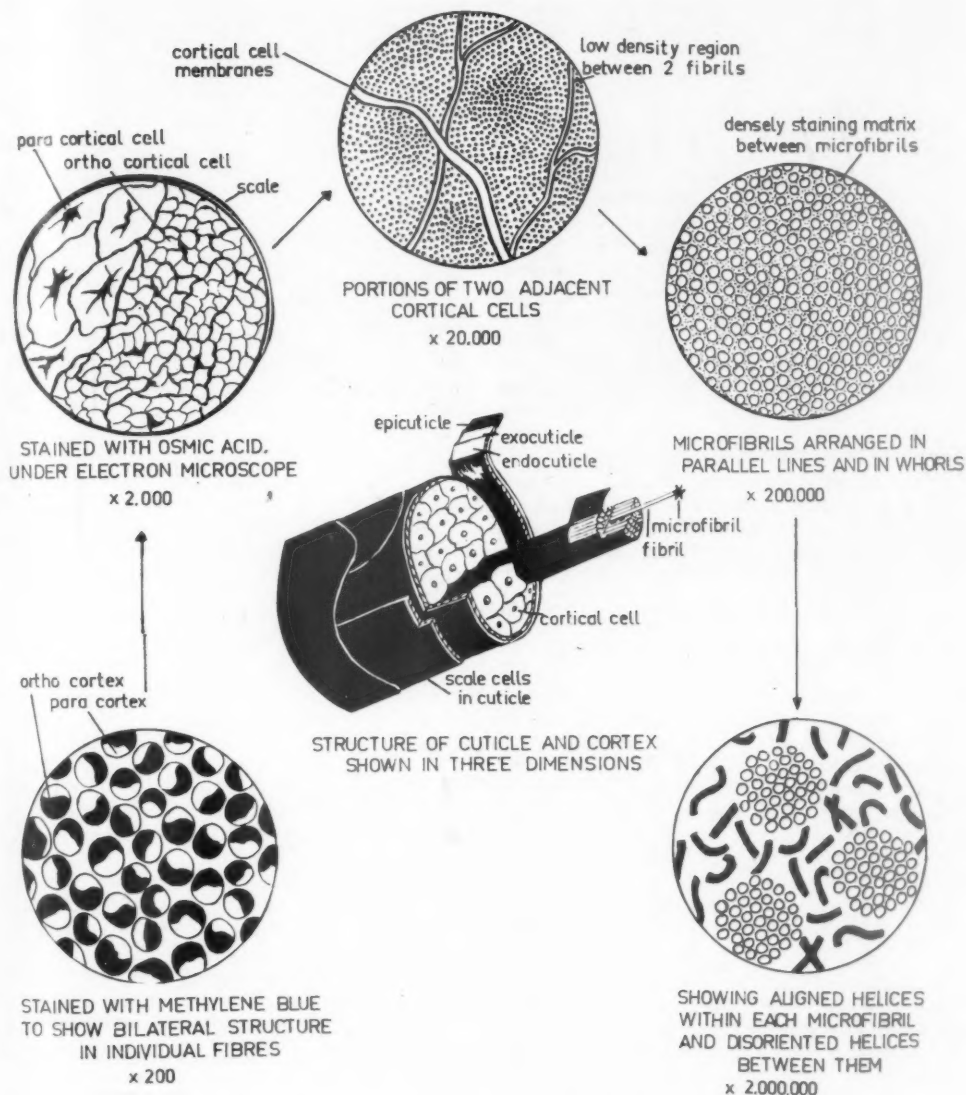
cortical cell membranes

low density region between 2 fibrils

para cortical cell
ortho cortical cell
scale

densely staining matrix between microfibrils

PORTIONS OF TWO ADJACENT CORTICAL CELLS
x 20.000

STAINED WITH OSMIC ACID. UNDER ELECTRON MICROSCOPE
x 2.000

MICROFIBRILS ARRANGED IN PARALLEL LINES AND IN WHORLS
x 200.000

epicuticle
exocuticle
endocuticle
microfibril
fibril
cortical cell
scale cells in cuticle

STRUCTURE OF CUTICLE AND CORTEX SHOWN IN THREE DIMENSIONS

ortho cortex
para cortex

STAINED WITH METHYLENE BLUE TO SHOW BILATERAL STRUCTURE IN INDIVIDUAL FIBRES
x 200

SHOWING ALIGNED HELICES WITHIN EACH MICROFIBRIL AND DISORIENTED HELICES BETWEEN THEM
x 2.000.000

Figure 5. Sketches showing cross-sections of merino wool at increasing magnification

to proteins in solution and several methods have been examined for extracting proteins from wool which use one reagent to split the disulphide bonds and another to disperse the product (see *Figure 6*).

Most of the wool proteins which have been studied in our laboratories have been extracted from wool either with alkaline thioglycollate, which reduces the –S–S– bonds, or with ammonia following oxidation of the –S–S– bonds with peracetic acid (α-keratose).   The purity of the thioglycollate extracts has been assessed by moving boundary electrophoresis[34,35], using thioglycollate in the

electrophoresis, buffers to prevent re-oxidation or following reaction of the –SH groups either with iodoacetic acid to form S-carboxymethyl (SCM) derivatives or with iodoacetamide. Other SH reagents are less satisfactory[36].

Partial purification of the wool proteins is achieved by five-fold extraction of wool with unbuffered thioglycollate at pH 10·5 followed by a single extraction with unbuffered thioglycollate initially at pH 12·2. Whereas the first extract shows at least four peaks on electrophoresis, the pH 12·2 extract shows a single peak (*Figure 7*). The physico-chemical properties of the SCM derivative solutions of the pH 12·2 extract, termed SCMK2, and of α-keratose depend on the time which elapses before testing and on the pH value and the salt concentration. Such variations appear to be due to aggregation–disaggregation reactions[37,38]. Some disaggregation is achieved by using high alkalinity, urea, sodium dodecyl sulphate[39], acetic acid or guanidine[40]. The properties of SCMK2 and α-keratose have also been measured in dissociating organic solvents such as formic acid and dichloroacetic acid[41]. Aggregation phenomena also probably

account for the variation in molecular weight from 12,000 to 16,000 of the wool proteins extracted with urea–bisulphite solution[42,43] and in the properties of the water-soluble wool proteins extracted with cuprammonium–sulphite solution[44] which are being investigated[45]. The second of the five successive pH 10·5 thioglycollate extracts of wool shows the highest molecular weight as measured on the surface balance[46] and yields the strongest of the protein filaments when the extracts are extruded into sulphuric acid–sodium sulphate solution[47].

Although aggregation complicates the assessment of purity[48], further fractionation of SCMK2 is achieved by precipitation with zinc acetate or by salting out with ammonium sulphate[49]. At pH 9 and low ionic strength both zinc-purified SCMK2 and α-keratose have a minimum molecular weight of about 9,000 as measured on the surface balance[50]. The N-terminal[51] and C-terminal[52] amino acids in SCMK2 are similar to those reported for wool and, being present in very small proportions, may represent impurities or breakage points in a collection of cyclic molecules. Alternatively, both N- and the C-terminal residues may be masked by substituents.
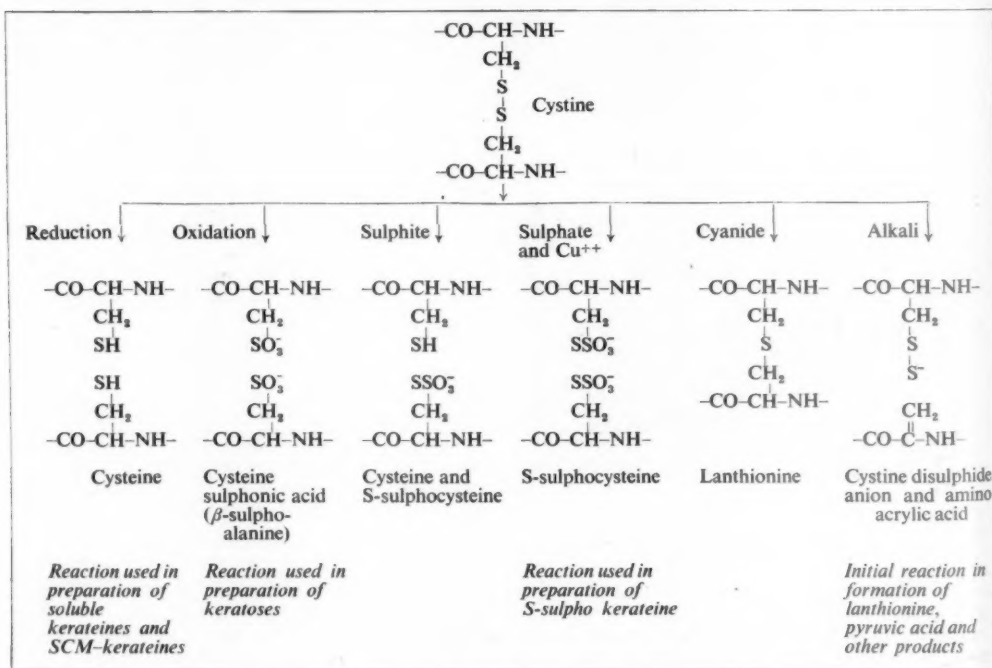

Figure 6. Reactions of the –S–S– bonds of cystine involved in the preparation of soluble wool proteins and in other chemical treatments of wool

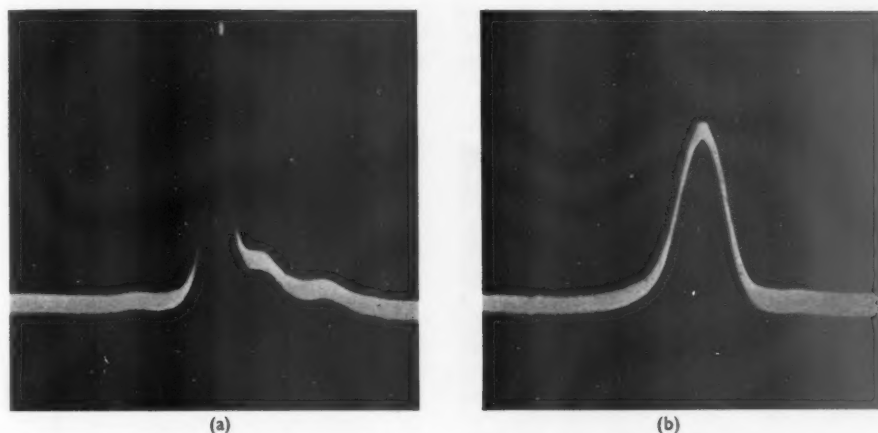(a)   (b)

Figure 7.   Electrophoresis diagrams of a thioglycollate extract of wool showing four protein components in (a) and the second component in (b) after purification by fractional precipitation

Fractionation of a pH 10·5 thioglycollate extract of wool yields a second protein derivative resembling SCMK2, *e.g.*, by containing much less sulphur than intact wool[53], and a third protein fraction with a high sulphur content which may originate in the sulphur-rich inter-microfibrillary matrix.

Alkaline thioglycollate extraction of proteins from wool is unlikely to cause serious peptide bond degradation for, although ammonia is released before peptide bonds are hydrolysed when asparagine peptides are heated in acid solution[54], no ammonia is liberated from wool during the thioglycollate extraction[55].   Moreover the dialysable nitrogen in the extracts is about ten per cent in the presence of thioglycollate[56] and not more than three per cent in its absence[57], and infra-red measurements show that the bulk of the protein extracted with pH 12·6 thioglycollate exists in the α configuration[58]. However, racemization of certain amino acids may occur during the extraction resulting in an increased complexity of the fragments obtained by tryptic digestion of the extracted protein[55].

The inadequacy of reduction of –S–S– bonds alone as a means of dissolving wool proteins and the important contribution to the insolubility of wool of such factors as chain configuration have been shown by treating wool ten times with thioglycollate, at pH 5·6 to avoid risk of splitting peptide bonds, and coupling the –SH groups formed in each treatment with iodoacetamide.   Although almost all the –S–S– and –SH groups are thereby eliminated, the product is not appreciably soluble[59] in buffer at pH 9·0 or 10·5.   It has long been assumed that only

alkaline solutions of thioglycollate and other thiols will dissolve wool proteins but acid solutions of thiols are also effective if the ionic strength is low[60].

Amino Acid Composition

Recognizing the need for rapid methods of estimating the amino acid composition of wool, wool proteins and peptides, ion exchange chromatography has been used for this purpose in its original form, with minor changes[61], and in fully automatic apparatus which graphs the absorption values[62]. In the latest model (*Figure 8*) eight columns feed eluate successively into a single photometer and the amino acid concentrations are printed on paper strips[63].   Using chromatographic methods, the amino acid composition of wool has been shown to vary from breed to breed and to a lesser extent from sheep to sheep, but not over the body of the same animal[64,65].

Amide side chains have been estimated either by chromatography, together with the amino acids or separately, by carefully controlled hydrolysis in 2N hydrochloric acid and distillation at pH 9 into boric acid solution[67]. Cysteine and cystine are best determined polarographically[68,69]. If samples weighing 10mg to 100mg are available, these are hydrolyzed and treated with sodium sulphite and excess mercuric chloride and the excess estimated using the dropping mercury electrode.   If only 0·05mg to 0·10mg samples of wool are available, for example single Merino fibres or short lengths of Lincoln fibres, the very sensitive catalytic wave produced by thiols in the presence of cobalt ions

is employed. A further improvement has enabled cystine and cysteine to be estimated in intact wool and has eliminated the variable loss of these amino acids which occurs during hydrolysis[68],[70]. To determine –S–S– plus –SH groups the sample is

Figure 8. Bank of pumps (on left) feeding buffer into columns and ninhydrin reagent dispenser (on right) operating in conjunction with fully automatic eight column machine for estimating the amino acid composition of wool and wool proteins

immersed for 18 to 24 hours in a buffered solution at pH 9 containing $8M$ urea to swell the fibres, also sodium sulphite and a mercurial such as neohydrin or mercuric chloride to react with the sulphydryl groups formed. Excess mercurial is measured polarographically (*Figure 9*). If –SH groups are to be estimated in the original wool, an excess of a monofunctional mercurial such as meohydrin or methyl mercury iodide is used in the absence of sulphite. Wools containing thioether groups, such as those which have been reduced and coupled with iodoacetic acid or iodoacetamide, yield cystine values up to four per cent too high if oxidized before hydrolysis[71].

Lanthionine in hydrolyzates may be estimated following oxidation with a mixture of hydrogen peroxide and ammonium molybdate, and cysteine plus cystine by oxidation of partial hydrolyzates with bromine followed by completion by hydrolysis. The oxidation products are separated by paper and column chromatography respectively[72].

Chemical Reactivity of Wool

The disulphide bond is the site of the most important reactions in wool chemistry. It is readily reduced[73] and when thioglycollate is used for this purpose some thioglycollate is bound to the wool apparently in the form of mixed disulphide[74]. The reduction in thioglycollate solution at pH 5 is

slightly increased by stretching wool fibres by about 90 per cent[75].

Alkali also splits disulphide bonds, and β-elimination has been postulated as the first step in the conversion of cystine to an organic disulphide anion and amino acrylic acid in the peptide chains[75]. The well known formation of lanthionine can be explained on the basis of β-elimination and the reported degradation of wool by diazomethane is believed to be due to the strong base tetramethyl ammonium hydroxide formed from the methyl-amine impurity present[77].

Cystine residues react with sodium sulphite to form one molecule each of combined cysteine and S-sulphocysteine ($RSSO_3H$), the latter being formerly known as S-cysteine sulphonate. But whereas the reaction at pH 5 with free cystine proceeds readily, only half of the combined cystine in wool ($A + B$ fraction) reacts in this way and, of this, half reverts to cystine on washing with water (sub-fraction *A*). Such reversal is prevented by esterifying the wool or by washing with a solution having a pH value below 4, and –COOH groups may therefore be implicated in the reverse reaction[78]. Of the cystine not reacting ($C + D$ fraction), one half (*C* sub-fraction) reacts if the temperature is raised. When the $A + B$ fraction is split with bisulphite the stress–strain curve of wool is only slightly affected, but when the $A + B$ links are replaced with stable cross links and the $C + D$ links then split, the Hookean region of the stress–strain curve is eliminated[79].

If a cupric salt and ammonia are added to the sodium sulphite solution, each cystine residue yields two S-sulphocysteine residues and much of the wool dissolves overnight to form S-sulpho-kerateine[44]. This product is readily converted into the thiocyanate derivative or mixed disulphides.

Solutions containing bisulphite[80] or thioglycollate[81], together with urea and a proteolytic enzyme such as papain to split peptide bonds, almost completely digest wool in a few hours at 60°C to 80°C. The extent of digestion is affected by previous modification of the fibre[82].

Another reaction involving the disulphide bonds is the formation of thiazolidine-4-carboxylic acid which occurs in hydrolyzates of wools previously heated above 70°C in the presence of formaldehyde. It seems probable however that this derivative is formed only during the hydrolysis stage[83].

The hydrocarbon side chains, together with other hydrophobic regions of the wool proteins, may represent sites for absorption of the various anions which promote supercontraction of the wool fibres.

The relative effects of the anions are in accordance with their positions in the lyotropic series, the least hydrated ions being the most effective[84]. After disordering the wool proteins by supercontraction in hot solutions of salts such as lithium chloride they are much more readily extracted with alkaline thioglycollate than before[85]. Heating in water has the reverse effect[57].

The hydroxyl groups attached to the serine and threonine residues in wool are surprisingly unreactive although they appear to be concerned in an acyl shift reaction when wool is heated with dry hydrogen chloride gas or with concentrated sulphuric acid as in the carbonizing process[86]. This reaction and the sulphation of these residues may explain the tendering and breakdown of wool fibres during carbonizing[87].

Side chains contributed by the basic amino acid residues of wool figure prominently in several reactions. It has long been known for example that the amount of the acid dye Orange II combining with wool is equivalent to all the basic residues, that
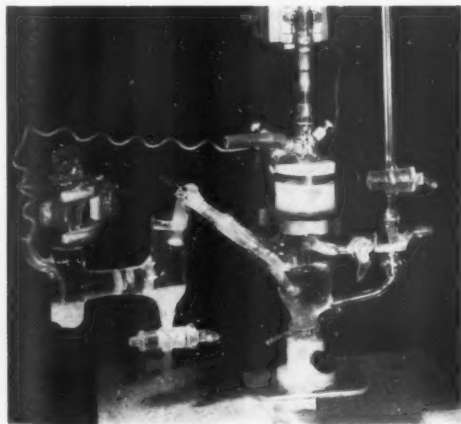

Figure 9. Polargraphic cell (on right) and calomel half cell used in the estimation of disulphide and sulphydryl groups in intact wool and proteins

is 0·88 milliequivalents per gram, but it has recently been shown that only 0·33 milliequivalents combine with the wool protein SCMK2 in solution[88]. This corresponds with the lysine plus histidine residues present and it is presumed that the arginine side chains are rendered inaccessible through aggregation of the wool protein molecules in solution. The dye molecules also react with a wool protein monolayer spread on the surface balance, the reaction increasing with increase in ionic strength due to penetration

into the monolayer[89]. The amount of sodium dodecyl sulphate combining with SCMK2 is equivalent to more than twice the total number of basic groups present[39]. Each detergent anion attached to a basic side chain in the wool protein is assumed to carry a second detergent molecule loosely bound to it. The quantity of zinc adsorbed on SCMK2 exceeds the histidine present and it is held less firmly than in insulin[90].

If particular peptide bonds in wool are hydrolysed, for example, by trypsin following partial disordering of the proteins in alkaline soap solutions, about ten per cent of the fibre is digested[91]. The peptide bonds are hydrolysed less specifically if wool is heated in solutions of weak acids or in dilute solutions of strong acids although up to 50 per cent of the available aspartic acid is then released preferentially by a unimolecular proton transfer mechanism[92]. Attempts to introduce additional peptide bonds into wool by reaction with cyclohexyl carbodiimide, which was expected to link together $-NH_2$ and $-COOH$ groups attached to neighbouring peptide chains, have been only partly successful[93].

Some Comments

One of the most puzzling features of research in the field of wool chemistry is the wide divergence between the reactivity of wool and of simpler compounds containing the same groups. Slow penetration of the reagents to the reaction sites is partly responsible, and this is associated with the low permeability of cuticular and cortical cell membranes, the lower permeability of the *para*-cortex than the *ortho*-cortex, and the existence of crystalline regions within the fibre, presumably in the microfibrils, allowing little space between the α-helices. Another factor is the influence of neighbouring groups on the reactivity of particular groups within the structure as distinct from their purely steric effects. Added to these considerations are the improved accessibility if the fibre is swollen before reagents are applied and the effect of the previous history of the fibre, such as hydrothermal treatment, on its reactivity.

Although these factors enormously complicate the task of elucidating the structure, chemistry and physics of wool, when adequately understood they should offer much more scope for exploiting the fibre than has been contemplated so far.

The author regrets that it has not been possible in this brief survey of recent advances in the Melbourne wool research laboratories to refer to the interesting work that is in progress in other laboratories both in Australia and in other countries.

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LARGE SCALE PREPARATION OF ULTRA-PURE SILICON

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GERMANIUM and silicon behave as semiconductors only when certain impurities are present. Control is achieved by producing material of extremely high purity and doping this with the requisite amount of the appropriate impurity element. Intrinsic germanium is available for this operation but intrinsic silicon has never been prepared. Hence the silicon material field is one of continuing development though for industrial reasons, but little information is being published. The silicon situation is obscure therefore in comparison with that for germanium.

Requirements

Semiconductor devices are produced from mono-crystals. It is essential therefore that silicon should be free from impurities which are insoluble in liquid silicon since these interfere with crystal growing processes.

All known requirements for monocrystalline germanium or silicon for semiconductor purposes revolve around the absence of most impurities and the presence of certain desirable ones. Among the parameters specified by the designers of devices is the resistivity. The relationship between the resistivity of silicon and the impurity concentration is shown in *Figure 1*. The impurities here are the electron-accepting elements of group III of the periodic table which give *p*-type material and the electron-donating elements of group V which render the material *n*-type. As a working rule it is sufficient to start with material which has a resistivity from 10 to 100 times higher than that of the doped material ultimately required. On this basis a starting resistivity of 100 to 1000 ohm cm is sufficient, but for high voltage rectifiers and some other devices a resistivity in excess of 1000 ohm cm is required.

The lifetime of the silicon monocrystals is also specified by the designer. Elements which affect the lifetime of the monocrystals should not be present: iron, copper and gold are known to behave in this way. Another requirement is that there should not be a catastrophic change of properties during the heat treatments which are unavoidable in the alloying and diffusion processes employed in device fabrication. Impurity elements which diffuse rapidly and degrade the resistivity or lifetime or cause thermal conversion from one conductivity type to the other must be absent. Copper and gold are known to be fast diffusers and oxygen plays a significant role in heat treatment phenomena.

It has not been an easy task even partly to meet these requirements and the difficulties have been mainly chemical in origin.

Difficulties in Preparing Pure Silicon

Silicon is one of the most reactive elements, reacting very easily with oxygen. The result is that it is always found in nature combined with oxygen in the form of silica or silicates. The great stability of the oxide requires drastic reducing conditions in the process used for extracting the element.

The normal silicon of commerce is obtained by the reduction of sand with coke at high temperatures in an electric furnace but the purity of the product is insufficient for semiconductor use. Other methods of production had to be employed and until recently these all involved the reduction of halogen compounds of silicon. Essentially the same problems as those encountered with the oxide arose and the reducing agents and the conditions required were so drastic that the compounds of many other elements present as impurities were reduced simultaneously. The final purity depended almost completely on the purity of the silicon halide and of the reducing agents. In addition the chemical engineering problems involved in dealing with halogen compounds at high temperatures are formidable when no contamination can be permitted.

The successful production of intrinsic germanium was due to the discovery of the physical zone refining process in addition to the chemical process. The reactivity of silicon has precluded the use of zone refining for silicon on a large scale because it has not been possible to find a container for the molten

element which did not contaminate it, although in the laboratory the process has been carried out without a crucible. The situation is further complicated by the fact that boron, which is a

troublesome impurity, distributes itself almost equally between solid and liquid silicon and cannot be removed by zone refining.

Fused quartz has been the crucible material with the least limitations but the overriding disability is that there is always some reaction between quartz and molten silicon so that it is impossible to obtain oxygen-free silicon when quartz crucibles are used.

Thus the high purity has had to be obtained by chemical and not physical methods and the purity has had to be maintained by crucible-free crystal growing processes.

Methods for Preparing Pure Silicon

Semiconductor grade silicon was first produced on a large scale by the du Pont Company in the United States by the vapour phase reduction of silicon tetrachloride with zinc and most of the silicon used is still produced by this method. Silicon tetrachloride has been used as the starting material for other processes and in some of these hydrogen was used as the reducing agent. The silicon produced has had a resistivity of only a few hundred ohm cm at the best. Other processes have also used silicochloroform, $SiHCl_3$ as the starting material.

Several years ago it was realized by some of the users that a superior grade of silicon was required.

This led to work in the United States, Germany and England on the decomposition of silicon tetraiodide, the reduction of silicochloroform and the thermal decomposition of silane, SiH_4. Two of these
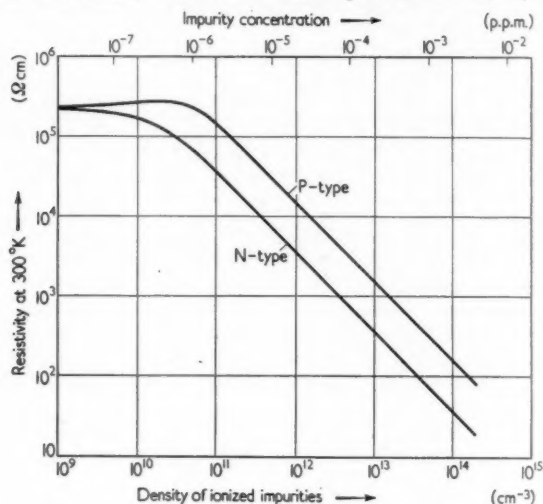

Figure 1. Relationship between the resistivity and impurity concentration of n- and p-type silicon[18] (by courtesy of Heywood and Co. Ltd)

processes, one developed by Siemens and Halske in Germany and the other by Standard Telecommunications Laboratories in England, are to be exploited on a large scale. Only the principles of these methods are clear.

Because of the varying amount of detail which has been published it is inevitable that any review of the production methods will appear unbalanced.

The du Pont Process

Our knowledge of the du Pont process is based upon the paper by D. W. LYON, C. M. OLSON and R. D. LEWIS[1]. Silicon tetrachloride is reduced with zinc in a fused quartz apparatus

$$SiCl_4 + 2Zn = Si + 2ZnCl_2.$$

Specially pure zinc and purified silicon tetrachloride are used as the starting materials and the vapours are fed into a reaction chamber held at 950°C. The zinc vapour is produced in a boiler heated to a temperature of 700°C and the silicon tetrachloride is vaporized and the vapour then heated to 650°C in a two stage system. Normally excess silicon tetrachloride is fed to the reactor.

Silicon is deposited in the reactor as needles, while any unreacted zinc and silicon tetrachloride, and the zinc chloride produced during the reaction, passes through an exit tube, heated to 1000°C, to the

collector chamber. The zinc and zinc chloride are retained there but the silicon tetrachloride passes on and is condensed subsequently.

The product requires further purification after removal from the chamber. It is inspected and sorted by hand, any silica, scale or other foreign matter being rejected. Large crystal conglomerates are crushed and the resulting material is digested with hot hydrochloric acid for twelve hours. The acid is diluted with water and the digestion continued for a further four hours. The silicon is then filtered, washed and dried. Treatment with a hot mixture of sulphuric and hydrofluoric acid gives metallic grey needles of silicon after filtering, washing and drying. The needles are often consolidated into a massive silicon, although the method employed is a matter for conjecture.

The Iodide Process

It is possible to obtain silicon by the thermal decomposition of silicon tetraiodide

$$SiI_4 \rightleftharpoons Si + 2I_2^4.$$
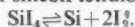
The method has received a great deal of attention despite the fact that the yield of silicon from 536 grams of silicon iodide is only 28 grams. The first comprehensive paper was that of F. B. LITTON and H. C. ANDERSON[2]. Silicon iodide was prepared by the reaction of resublimed iodine and commercial 'high purity' silicon at 800°C and subsequently purified by fractional distillation from a quartz still. The iodide was decomposed on a tantalum wire helix heated to a temperature of 1000°C in a quartz tube connected to a vacuum system.

Workers seeking to improve this process have concentrated on the purification and decomposition of the iodide. G. McCARTY introduced the step of recrystallizing the silicon iodide before distilling it. B. RUBIN et al.[3], who have also investigated the iodide method, obtained a purer silicon tetraiodide by physicochemical methods. The iodide was purified in three stages: by recrystallization from fractionally distilled toluene, by sublimation and finally by zone refining. C. S. HERRICK and S. G. KRIEBLE[4] constructed a pilot plant unit based on the work of McCarty. Silicon iodide is formed from silicon and iodine in a fluid bed reactor and it is purified by recrystallization from n-heptane followed by distillation in a quartz column. Their process is an improvement in that the silicon tetraiodide is decomposed on a silicon rod heated to 1000°C.

Reduction of SiCl₄ and SiHCl₃

Although silicochloroform is produced on the large scale from silicon and hydrogen chloride, it can be obtained by the reduction of silicon tetrachloride with hydrogen at high temperatures

$$SiCl_4 + H_2 = SiHCl_3 + HCl.$$
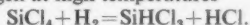
It is not surprising therefore that the reduction of silicon tetrachloride and silicochloroform can be conducted under similar conditions. Both processes have been used on a large scale, the silicon being deposited in quartz tubes heated to about 1100°C,

$$SiHCl_3 + H_2 = Si + 3HCl$$
$$SiCl_4 + 2H_2 = Si + 4HCl.$$
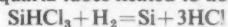
The silicon adheres to the quartz so that contamination arises at the decomposition stage and in the subsequent operations for the removal of the quartz. It is an advantage to produce the silicon in the form of rods. The methods employed stem from the work of A. E. VAN ARKEL[5] who reported the reduction of various silicon compounds including silicon tetraiodide, silicon tetrachloride and silane on hot tungsten filaments.

In the case of silicon tetrachloride the process was carried a step further by H. C. THEUERER[6] who passed a controlled mixture of purified hydrogen and silicon tetrachloride over a tantalum tape heated to 1100°C. The thin silicon rod thus produced is cut longitudinally and the tantalum core dissolved in hydrofluoric acid. Theuerer's process has not been used on a large scale.

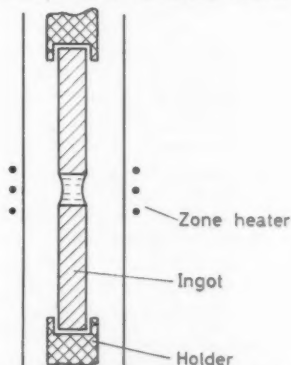In the Siemens and Halske process, as described by E. SPENKE[7], a mixture of silicochloroform and

Figure 2. Floating zone technique—reproduced from Preparation of Single Crystals *by* W. D. LAWSON *and* S. NIELSEN *(Butterworth Scientific Publications, 1958)*

hydrogen is passed over a silicon rod heated to about 1000°C by passing a current through it. The silicon produced is thus deposited on the silicon rod and this is an obvious advance. It appears from the patent specification[8] that the mixture of silicochloroform and hydrogen is reacted in an electric discharge between two silicon electrodes in a glass or quartz water cooled chamber, the temperature of
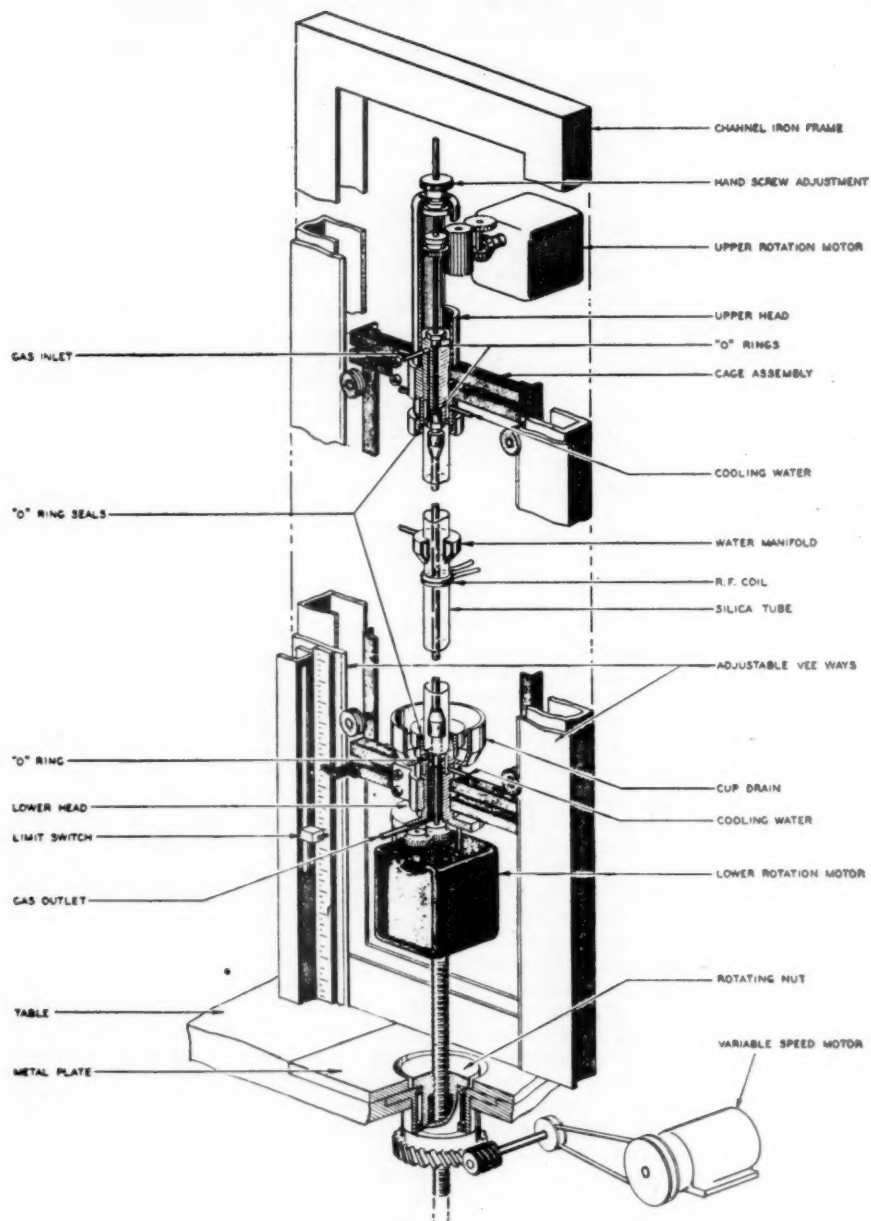
CHANNEL IRON FRAME

HAND SCREW ADJUSTMENT

UPPER ROTATION MOTOR

UPPER HEAD

"O" RINGS

CAGE ASSEMBLY

GAS INLET

COOLING WATER

"O" RING SEALS

WATER MANIFOLD

R.F. COIL

SILICA TUBE

ADJUSTABLE VEE WAYS

"O" RING

CUP DRAIN

LOWER HEAD

COOLING WATER

LIMIT SWITCH

LOWER ROTATION MOTOR

GAS OUTLET

ROTATING NUT

TABLE

VARIABLE SPEED MOTOR

METAL PLATE

*Figure 3. Arrangement of mechanical parts of floating zone refining apparatus
—reproduced from* Rev. sci. Instrum. 28 (1957) 455

the discharge being regulated so that the reaction occurs but the silicon produced is deposited in the form of a molten mass on one electrode and cools to a crystalline mass. The rod is automatically withdrawn as it is built up. A high voltage (1000 to 10,000 volts) is required between the electrodes but the discharge may be operated by either a.c. or d.c. The floating zone process may be applied to the rod produced either in situ or after removal from the chamber.

Purity of the Product

The purity of the product from these methods is limited by the purity of the silicon compound and the reducing agent because most impurity compounds likely to be present are also reduced under the conditions required for the reduction to the silicon. Zone refining which is used for germanium does not provide the complete solution for silicon because boron cannot be removed; boron is almost equally distributed between liquid and solid silicon, the distribution coefficient being above 0·8. It is most important therefore that the required boron content is obtained prior to zone purification.

We have referred earlier to the reaction of molten silicon with all known crucible materials and the development of the floating zone process. In this process a narrow molten zone, produced by high frequency heating and supported by surface tension, is passed through a rod rigidly held at both ends and mounted vertically (*Figure 2*). By moving the rod or the heating coil the zone is made to pass through the length of the rod. If the process is repeated most impurities are removed, boron being a notable exception, and for this reason the refined silicon is *p*-type.

Although the silicon produced by Spenke and Theuerer was similar before refining, both being *n*-type with a resistivity of 50 ohm cm and 100 to 150 ohm/cm respectively, that of Spenke had a boron content of 10^{13} atoms/cc corresponding to resistivities up to 1000 ohm cm after the floating zone treatment compared with Theuerer's 10^{14} atoms/cc and a few hundred ohm cm. In order to obtain a lower boron content Theuerer[9] had to introduce another process. He found that boron was removed by allowing hydrogen and water vapour to react with the silicon in the molten zone. E. BUEHLER[10] reports that after this treatment and 67 floating zone passes the silicon had a resistivity of 16,000 ohm cm corresponding to a boron level of less than 10^{13} atoms/cc. Buehler's apparatus is shown in *Figure 3*.

This final purification based on the floating zone process, whether in argon, vacuum or wet hydrogen, is a disadvantage for any large scale process. The

silane method is attractive because the purification is carried out before the silicon is produced.

The Silane Process

It is possible after studying the principles and the results of the methods already described to draw the general conclusion that unless a major purification is an inherent feature of the method itself the reactants must be of semiconductor purity and further that the difficulties are multiplied by the number of reactants.

The Silane Silicon process developed by Standard Telecommunications Laboratories[11–13] uses the thermal decomposition of a gaseous silicon compound, since in general it is easier to purify a gas than either a liquid or a solid. Silane, silicon hydride, SiH_4, which melts at $-184°C$ and boils at $-112°C$, is thermodynamically one of the most stable of the volatile hydrides, but it decomposes above about $500°C$, forming silicon and hydrogen only. No difficult problems connected with the materials of construction of the apparatus arise, since silane and hydrogen are relatively unreactive gases. Economically the thermal decomposition of silane is attractive since 28 grams of silicon are obtained from only 32 grams of silane,

$$SiH_4 = Si + 2H_2.$$
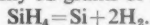
The silane is generated by the reaction of lithium aluminium hydride and silicon tetrachloride in diethyl ether or tetrahydrofuran

$$LiAlH_4 + SiCl_4 = SiH_4 + LiCl + AlCl_3.$$
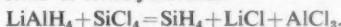
By employing this general method for the preparation of hydrides, which is due to A. E. FINHOLT *et al.*[14], an immediate purification is obtained. By retaining non-volatile reactants and products in the generator only the volatile hydrides leave and these are formed only by the elements of the B subgroups of the periodic classification from group III and higher. The impurity elements are limited to those whose hydrides are volatile at the temperatures and pressures in the generation system and these can be dealt with specifically, being removed from the reactants or the silane gas.

In addition, boron present as an impurity in the reagents can be converted to lithium borohydride which is not volatile, if there is excess silicon tetrachloride present during the reaction. This follows from the work of I. SHAPIRO and H. C. WEISS[15] who showed that diborane, B_2H_6, is only formed from lithium aluminium hydride and boron trichloride when all the lithium aluminium hydride has been converted to the borohydride,

$$LiAlH_4 + BCl_3 = LiBH_4 + AlCl_3$$
$$3LiBH_4 + BCl_3 = 3LiCl + 2B_2H_6.$$

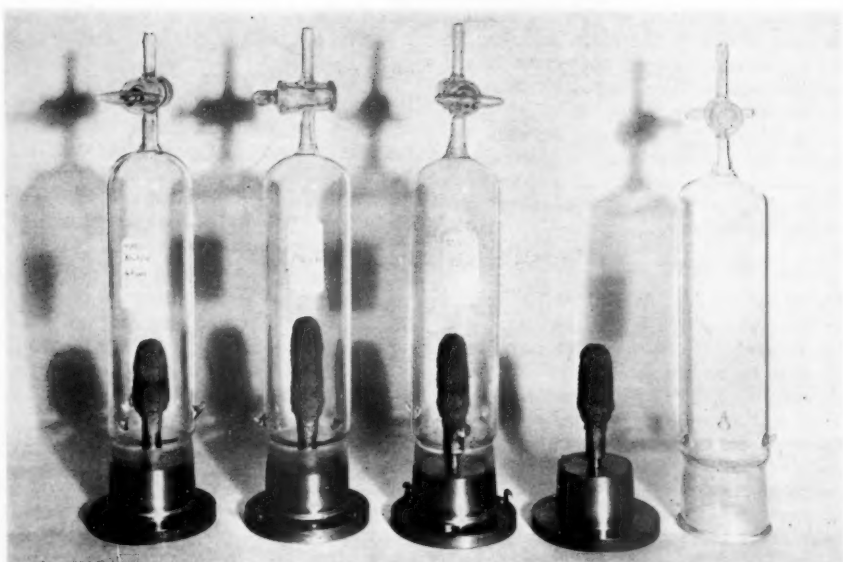Under suitable conditions silane can be made to

Figure 4.   Ultra-pure silicon prepared by decomposition of silane (by courtesy of Heywood and Co. Ltd)

decompose by a surface reaction and H. F. STERLING of these laboratories has developed a special form of radiofrequency heating which allows us to obtain a hot silicon surface which essentially is the only hot object in the decomposition system. It is thus possible to conduct the decomposition on a hot silicon surface and to build up a massive silicon. Some small samples are shown in *Figure 4*.

A crucible free crystal pulling process has been developed at the Standard Telecommunications Laboratories by F. J. Raymond and H. F. Sterling which allows the silicon boules to be converted to monocrystals without using a crucible.   Single crystals are pulled from a molten pool maintained on the top of a boule, the position of the molten region being maintained constant relative to the R.F. coil by raising the boule and feeding in material as fast as the pool is depleted.   Using this method *p*-type single crystals of silane silicon with several thousands of ohm cm resistivity and life-times of a millisecond have been obtained.

Production Forecasts

The scale of operations is not clear from the description of the processes which is available.   It is interesting therefore to consider that an estimate of production in the United States for 1960 is 100,000 lb of semiconductor silicon and that J. K. KENDALL[16] has estimated the usage in the United Kingdom to be 10,000 lb by 1960.   These give some idea of the

limited output of silicon which may be required for the mass production of diodes and transistors since the amount of silion in each device is small.

In conclusion we may remark that whereas physical methods revolutionized germanium purification and technology, for silicon the necessity for eliminating the crucible and the absence of a physical method of purification suitable for industrial use has led to an emphasis on chemical methods.

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PRESSURIZED PACKAGING

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This article which surveys the history and the various techniques used for making pressurized packs is based on some sections of the book, *Pressurized Packaging (Aerosols)*, by A. HERZKA and J. PICKTHALL*, published by Butterworths Scientific Publications in November 1958.

THE growth and development of the pressurized packaging industry has probably been one of the most rapid developments in the history of technology. Somewhat more than half a billion pressurized packages had been produced in the United States up to the end of 1957 and W. E. GRAHAM[1] predicted an output of 500 million for 1958. The sales of shaving cream in the form of pressurized packs was nil in 1950 and had reached 51 million units by 1957, taking more than half the dollar market from old established products and also increasing the total sales substantially[2]. In the United Kingdom half a million packs were produced in 1950 compared with approximately sixteen million during 1958.

Unfortunately the word ' aerosol ' has become associated with this method of packing; aerosol is a term employed in colloid chemistry and has been defined[3] as a colloidal system consisting of very finely subdivided liquid or solid particles dispersed in and surrounded by a gas. In the early 1940s, the word aerosol was first used, or rather misused, to describe insecticides packed in a self-pressurized pack and from this, the following definition[4] of an aerosol product was evolved:

' A self-contained sprayable product in which the propellant force is supplied by a liquefied gas. Includes space, residual, surface coating, foam and various other types of product, but does not include gas-pressurized products such as whipping cream. The term aerosol as used here is not confined to the scientific definition.'

A much more satisfactory term is ' pressurized pack ' which may be defined as:

'a self-contained pack which contains the product and the propellant necessary for the expulsion of the former'.

This definition includes packs where the propellant force is supplied by compressed gases and, by discarding the term aerosol, it acknowledges that this word has a definite scientific meaning. Confusion is also avoided with the Aerosols[5], a series of surface active agents, and with aerosol therapy[6], an accepted form of medical treatment.

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History

The oldest record of a product being propelled by the dynamic energy derived from the pressure of its contents appears to be contained[7] in a patent of 1889. The inventors used methyl and ethyl chlorides, making a solution with either or both of these materials with or without the addition of alcohol or ether. The patent states:

' This solution is placed, with a considerable excess of methyl or ethyl chloride, if required, in a receiver of glass or metal having a suitable orifice which can be hermetically sealed at will with a close fitting cap. When it is required to make use of the solution, the cap is removed and the vessel inclined as may be necessary. The heat of the hand holding the vessel, or even of the surrounding atmosphere if of the ordinary temperature of the room, then immediately causes the ethyl or methyl chloride inside the receiver to begin to evaporate. This evaporation causes internal pressure, and the solution is thereby ejected through the orifice in a fine jet or spray.'

Soon after, the first of the Gebauer patents appeared[8], followed by a second[9] in 1908 in which certain improvements to the original container are described. At the end of 1903, R. W. Moore was granted a patent for a perfume dispenser[10], with carbon dioxide as the propellant. In 1921, L. K. Mobley[11] took out a patent for dispensing liquid antiseptics with carbon dioxide once more as the propellant. Methyl chloride was first mentioned as a suitable propellant in a German patent dated 1931 and in that year, E. Rotheim was granted his first patent[12], followed two years later by a second[13] which mentioned methyl chloride, *iso*butane, vinyl chloride and other materials as likely propellants in addition to dimethyl ether; the products mentioned as likely to be dispensed by this method are cellulose lacquers, rubber, gums, insecticides, polishes, fertilizers, fire extinguishers and cosmetics.

In 1933 a patent was taken out by T. Midgley, A. L. Henne and R. R. McNary[14] for a fire extinguisher which used fluorinated hydrocarbons as the extinguisher and in which dichlorodifluoromethane is specifically mentioned. This material had

been synthesized a short time previously[15] as a result of a research project to develop new and improved refrigerants to replace sulphur dioxide and ammonia. The discovery of the modern fluorinated propellants can be said to be the most significant contribution to pressurized packing as it is known today.

Research carried out for the United States Department of Agriculture during World War II in their efforts to combat the insects which caused discomfort to troops stationed in the Far East led to the development of the portable dispenser as depicted in *Figure 1*. Heavy metal containers were filled with insecticides and dichlorodifluoromethane and thus had to withstand pressures of the order of 70 p.s.i.g. at room temperature. Although costly and cumbersome, dispensers of this type were put on the civilian market[16] in 1945, but the industry was insignificant until the advent of a dispenser based on the tinplate beer can with soldered side seam and with a dispensing valve inserted in a concave end[17], in which systems having internal pressures of the order of 35 p.s.i.g. at 70°F were packed; a drawn steel container, having no side seam, and an aluminium container were also used. Since these early pioneering days, glass as well as plastic dispensers have come to the fore.

Figure 1. Insecticide bomb of dichlorodifluoromethane produced during World War II

Propellants

The majority of pressurized packs marketed up to now have utilized liquefied gas propellants; chlorofluorohydrocarbons, ethane and methane derivatives, form the largest and safest group. The advantage of using a liquefied gas as the propellant is due to the fact that the pressure within the pack is determined principally by the vapour pressure of the propellant and not by its quantity and the pressure within the pack will therefore remain constant as long as a single drop of liquid propellant remains.

Table 1. Liquid propellants used in the United Kingdom —the figures in italics denote inches of mercury vacuum

Chemical name	Trade name	Gauge pressure at 70°F
Chlorodifluoromethane	Arcton 4	122·5 p.s.i.
Propane	—	110·1 p.s.i.
Dichlorodifluoromethane	Algofrene 2 Arcton 6 Freon 12 Isceon 122	70·12 p.s.i.
Butane (commercial)	—	17–35 p.s.i.
Dichlorotetrafluoroethane (symmetrical)	Arcton 33 Freon 114 Isceon 224	12·87 p.s.i.
Trichlorofluoromethane	Algofrene 1 Freon 11 Arcton 9 Isceon 131	*2·64*
Methylene chloride	—	*7·9*
Trichlorotrifluoroethane	Freon 113 Arcton 63 Isceon 233	*18·68*

A list of liquid propellants commonly employed in the United Kingdom is given in *Table 1*, together with the relevant trade names and gauge pressures. The most commonly used propellant mixture consists of a mixture of dichlorodifluoromethane and trichlorofluoromethane, usually in equal proportions.

In addition to the liquefied propellants, compressed gases have also been utilized, hitherto chiefly for food products where nitrous oxide/carbon dioxide mixtures have been employed in the main. These gases are examples of propellants which are soluble in the product. Nitrogen, a compressed gas insoluble in almost every product, has recently been introduced for pressurizing toothpaste and other viscous products. The disadvantage of utilizing compressed gases lies in the fact that the pressure in the dispenser depends on the total amount of gas compressed within a given headspace. As the pack is emptied, the headspace will increase with a proportional decrease in the internal pressure, and ultimately the remaining pressure may be insufficient to expel the whole of the contents.

Method of Operation: Two-Phase System

The majority of pressurized packs are two-phase systems, *i.e.*, they consist of a single liquid or solid phase and a single vapour phase. The single solid phase consists only of product and the liquid phase
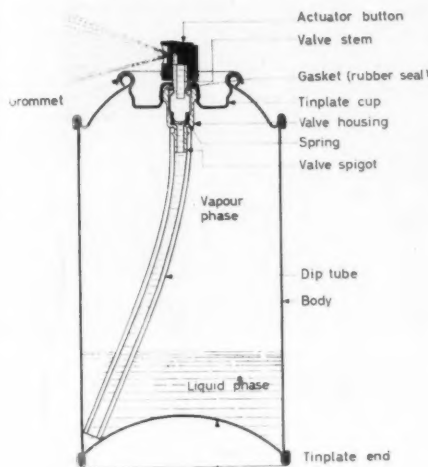

Figure 2. Precision valve dispenser with open valve

may consist of one of the following

   (*i*) product alone;

   (*ii*) a mixture of product and liquid propellant; or

   (*iii*) product containing dissolved propellant.

In (*ii*) where the liquid phase contains a mixture of product and liquid propellant, part of the latter vaporizes and the vapour phase thus created exerts its pressure not only against the walls of the container, but also against the liquid phase, thereby forcing the latter up the dip tube as far as the valve orifice. When the actuator button is depressed, the liquid phase passes first through the valve orifice and then into the atmosphere via the valve stem and button orifice (*Figure 2*). The liquid phase continues to be propelled forward as long as the valve is actuated and until the last drop of liquefied gas propellant vaporizes within the dispenser. The boiling point of the propellant or propellant mixture is usually far below ambient temperature and the propellant therefore vaporizes instantly on coming into contact with the atmosphere.

The majority of pressurized packs manufactured to date are of type (*ii*) and the relative amounts of product and propellant determine the nature of the resultant spray. If the amount of propellant

present is large, then *space sprays* result with the particle size of the order of 50 microns. If the amount of product approximately equals the amount of propellant, then *surface sprays* result. They are thus called because the particles can no longer remain airborne on account of their size, which is of the order of 100 to 200 microns. Hair lacquers are examples of the most successful pressurized surface spray and paints, varnishes, mothproofers, and lubricating oils are other examples.

When the liquid phase consists only of product, *i.e.*, type (*i*), then the headspace is filled with a compressed gas and when the valve is opened it forces the product up the dip tube and out of the valve. In such cases the propellant itself has no scattering effect on the product particles which will emerge as a thin jet unless the special break-up spray valves, referred to below, are employed.

Method of Operation: Three-Phase System

Three-phase systems give rise not only to space and surface sprays, but also to foams. In addition to the gaseous propellant phase, they consist either of two liquid phases which might be emulsified or one liquid and one solid phase. *Figures 3a* and *3b* depict three-phase systems having two distinct liquid layers. In such cases the product is usually water-based. When
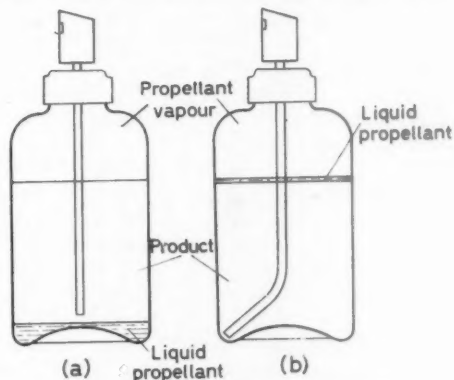

*Figure 3. Three-phase systems with two distinct liquid layers*

the valve is actuated, the pressure exerted by the propellant vapour in the headspace forces pure product up the dip tube and out of the valve. Special valve actuators, as previously mentioned, are required to break up the coarse product particles. If the specific gravity of the propellant exceeds that of the product the conditions shown in *Figure 3a* occur. Sometimes glass chips or porous pot fragments are added in order to promote the vaporiza-

tion of the liquid propellant. If the specific gravity of the propellant is less than that of the product, the conditions are as shown in *Figure 3b*.

Foam packs are three-phase systems where the liquid propellant, which normally does not exceed 15 per cent by weight, is emulsified with the product. When the valve is actuated, the emulsion is forced up the dip tube, where fitted, and out of the foam head (*Figure 4*). As soon as the emulsion contacts the atmosphere, the propellant particles within it immediately vaporize, whipping the whole into a thick foam of innumerable particles. (Shaving cream and furniture polish are examples of pressurized foam packs.) If no dip tube is fitted, then the dispenser is inverted during use. The foam quality can be varied by altering the type and amount of propellant.

In some three-phase systems, the propellant is only partially emulsified with the product and such packs are intermediate between the perfect three-phase systems and the foam packs described above. Such conditions may occur in glass cleaner formulations. Another type of three-phase system is the pressurized powder pack which consists of a vapour, a liquid and a solid phase. The liquid phase is normally pure
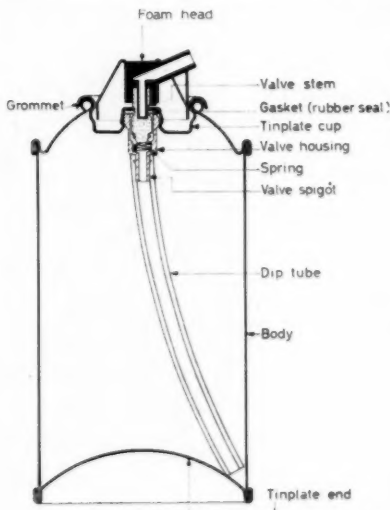
Figure 4. Dispenser fitted with foam valve

propellant, but may also contain a small amount of lubricant. Before use, the dispenser is shaken in order to disperse the powder throughout the liquid phase. The lubricant is added in order to aid the passage of the powder through the valve orifice(s).

Dispenser Components

Every pressurized dispenser consists of a container, a valve and diverse ancillary components. The following containers are generally available in Great Britain.

Figure 5. Plastic coated glass dispenser (2 oz) with internal pressure 28 p.s.i.g.—this dispenser broke when dropped on to a steel plate from a height of 6½ feet

Aluminium—Aluminium containers are commonly used for cosmetic products when external appearance rather than cost is the determining factor. Aluminium containers have the advantage over tinplate containers that the walls may be bulged, fluted, ribbed or formed to individual artistic conceptions. Aluminium containers are, unfortunately, prone to corrosion, particularly by the ingredients of many cosmetic preparations. Adequate internal lacquering, however, can usually overcome these difficulties.

Tinplate containers—Most products can be packed satisfactorily in internally plain tinplate containers, which are generally cheaper than those made of aluminium. The salient difference in construction is the soldered side seam in the former which causes a strip approximately one inch wide to be bereft of external decoration which, however, is not necessarily a drawback if the design of the external decoration is executed in a competent manner.

Glass containers—Glass containers are used chiefly for cosmetic products and the packs are formulated in such a manner that the internal pressure does not exceed 25 p.s.i.g. at 70°F. Nevertheless there is an ever present danger of explosive breakage, so thoroughly demonstrated by J. PICKTHALL[18], if naked glass containers are utilized. In Great Britain, at any rate, all glass dispensers are provided with a protective outer covering of either plastic or metallic nature. The effects of dropping a plastic coated glass dispenser and a naked glass dispenser on to a
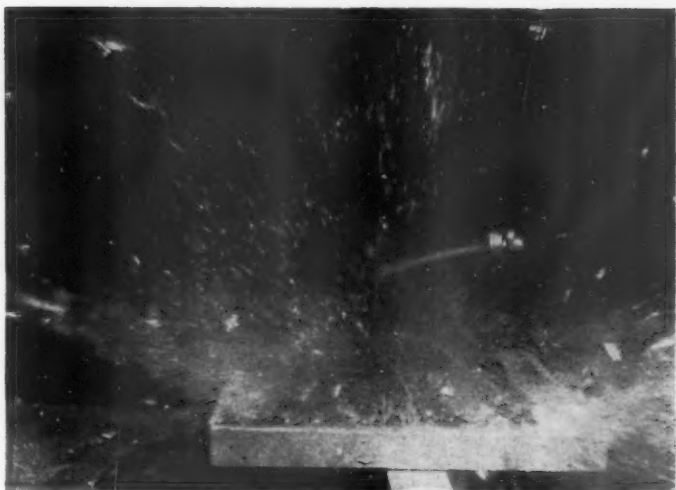
Figure 6. Uncoated glass dispenser (2 oz) with an internal pressure of
28 p.s.i.g. which was dropped on to a steel plate from a height of 6½ feet

steel plate from a height of six and a half feet are illustrated by *Figures 5* and *6*.

Plastic containers—These have already been test marketed in the United Kingdom.

Valves

It is through the valve that the product is obtained and the valve mechanism may therefore be considered a critical a part of the pack as the propellant. The majority of valves may be classified into six broad groups.

Standard valves—Standard valves are those which give a continuous emission while the actuator button is operated and as they form an integral part of the dispensers, they are discarded together with the latter when the product is used up (*Figure 2*).

Standard valves may be fitted with ordinary buttons suitable for all types of space and surface sprays, where liquid propellant is part of the liquid phase, providing the internal pressure of the pack is not much below 30 p.s.i.g. at 70°F. Alternatively, break-up spray buttons may be fitted. These are necessary for two-phase systems where the liquid phase consists only of product, for three-phase systems other than foams, and for all liquid sprays with low internal pressures. Atomization is achieved by forcing the product stream through a swirling chamber in the actuator button which causes a turbulence in the liquid stream as it passes to the final orifice, where it breaks up into fine particles which are, however, coarser than the particles obtained by propellant atomization (*Figure 7*).

Foam valves—These are designed for use with aerated emission (*Figure 4*).

Metering valves—Metering valves deliver equal dosages at each operation. Their uniqueness lies in the delivery of a predetermined quantity of material which is of definite economic interest because the administration of therapeutic dosages with pharmaceutical preparations is made possible.

Re-usable valves—These as their name implies, may be re-used on full dispensers after the empty dispensers have been discarded.

Toothpaste valves—Although primarily designed for packing toothpaste with compressed gas propellants, toothpaste valves may be used for all types of viscous products. They are characterized by having considerably enlarged orifices throughout the valve structure.

One-shot valves—These valves are chiefly employed for fire extinguishers for they permit the discharge of the whole contents of the dispensers at one time.

Advantages of Pressurized Packs

The advantages of pressurized packs may be summarized as: speed, ease and convenience of application; efficiency of dispersion; elimination of contamination of product with foreign materials; absence of air within dispenser; and others, depending on the particular product group.

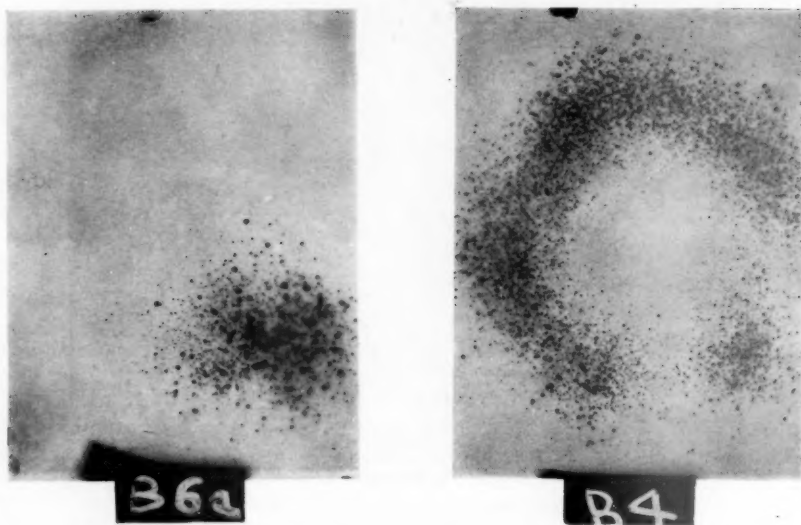With medicinal preparations, for instance, pressurized packs permit direct local application of a high

Figure 7. Spray pattern obtained with hair lacquer packed in the proportion 65 per cent hair lacquer solution and 35 per cent dichlorofluoromethane—(a) using a standard valve with an ordinary button and (b) using standard valve with break-up spray button

concentration of drugs. The application can also be made without touching painful areas. R. MYLES GIBSON[19] reports that the application of the antibiotic triad polymyxin, neomycin, and bacitracin in surgical practice which requires special consideration on account of the triad's relative insolubility and instability in aqueous solutions has been made possible by suspending the antibiotics in dichlorotetrafluoroethane and discharging in pressurized form.

Pressurized dispensing does an old job in a better way—the removal of paints and varnishes. The principal advantage of applying paint removers in this fashion are: application is easier and cleaner; less paint remover is required; the activity of the remover is increased by the ' slushy ' snow-like deposit obtained by skilful formulation, which tends to hold the solvents in close contact with the paint or varnish. Varnish softened by such a deposit can be easily and cleanly scraped off with a putty knife because the softened varnish tends to adhere to the deposit.

There are, of course, hundreds of products which may be packed in pressurized dispensers, because this method offers advantages over other forms of packing and it is quite impossible to detail all of

them. Suffice it only to say that this is a method of packing which deserves the earnest consideration of everyone.

The illustrations are reproduced from Pressurized Packaging (Aerosols) *by A. Herzka and J. Pickthall (London: Butterworths Scientific Publications, 1958)*

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PRODUCTION AND MEASUREMENT OF ULTRA-HIGH VACUA

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Recent experiments which have lead to the development of ultra-high vacuum systems, in which residual gas pressures as low as 10^{-10} mm Hg are obtained and measured by means of a combined ionization pump and gauge, are described; some of the applications of such systems are briefly outlined.

MANY of the advances during the past 50 years in pure and applied science have been dependent on the production of a high degree of evacuation of a suitable vessel. For the successful operation of devices such as radio valves, television tubes, x-ray machines, particle accelerators, electron microscopes, and many others, the establishment of a high vacuum is essential. It is clear that any new advance in the techniques for producing high vacua is likely to be of wide general interest, and the purpose of this paper is to describe some of the considerable developments which have occurred in this field in the last decade.

It is convenient for present purposes to classify vacuum systems into two general types. First, there are the systems in which it is possible to reduce the residual gas pressure to about 10^{-7} mm Hg; such systems will be called high vacuum systems. Second, there are the systems in which it is possible to obtain residual gas pressures as low as 10^{-10} mm Hg; this type of system will be called an ultra-high vacuum system, and it is with the recent experiments which lead to their development that this paper is mainly concerned. To understand the significance of these experiments, however, it is first necessary to outline the principles of the operation of the more conventional high vacuum systems. (An ultra-high vacuum system in use for experiments on ionization physics at the Department of Physics, University College of Swansea is shown in *Figure 1*.)

High Vacuum Systems

It has been possible for many years to obtain readily a residual gas pressure of about 10^{-6} to 10^{-7} mm Hg in systems such as that shown in *Figure 2*, provided certain precautions are taken. The main precautions necessary are:

(*i*) to ensure the absence of pin-holes which allow air to leak into the system from the atmosphere;

(*ii*) to ensure the removal of gases adsorbed on to the walls of the system (de-gassing), by heating the system for a long period to as high a temperature as possible with the pumps operating; and

(*iii*) to use only special greases and oils with a very low vapour pressure in taps and pumps, and to reduce the vapour pressure still further by means of cold traps placed between the source of vapour and the vessel to be evacuated.

The measurement of very low pressures ($< 10^{-3}$ mm Hg) encountered in high vacua requires the use of special techniques, and a wide variety of gauges has, in fact, been developed to operate in this range. The only gauge which is relevant to the present discussion, however, is the ionization gauge, the principles of which will now be described.

The Ionization Gauge

This gauge consists of an arrangement of electrodes similar to that in a triode radio valve, mounted inside a glass envelope which is attached to the vacuum system. The three electrodes are normally arranged as in *Figure 3a*; there is a straight wire filament F, surrounded by two concentric cylindrical electrodes, a meshed anode A and a solid collector C. In operation, the cathode is heated by passing a current through it, and gives off electrons which are attracted to the anode on account of the high (about 150 to 200 volts) positive potential maintained between anode and cathode. Some of the electrons penetrate into the space between the anode and the collector and there collide with and ionize molecules of the gas before being drawn back to the anode. The positive ions formed by the ionizing collisions will be attracted to the collector, because it is maintained at a small (about 20 volts) potential negative with respect to the cathode. The net effect is that in unit time a number, n say, negatively charged electrons flow to the anode and a number, N say, positive ions flow to the collector. The ratio N/n is a measure of the number of ionizing collisions made by each electron in the space between the collector and anode.

At the low pressures here considered, the number of ionizing collisions made by one electron depends on the number of gas molecules present, *i.e.*, on the gas pressure. Thus if the currents—proportional

to the number of charged particles arriving in unit time—to the anode and collector are measured, their ratio gives a measure of the pressure.

Figure 1. An ultra-high vacuum system in use for experiments on ionization physics in the Department of Physics, University College of Swansea—M, all-metal, greaseless ultra-high vacuum tap; V, vessel to be evacuated; I, ionization gauge and pump; P, power supplies for gauge; L, screened lead from ionization gauge to an electrometer for measurement of current

Such an ionization gauge can be used to measure gas pressures as low as 10^{-7} mm Hg, a pressure which can be measured by only one other type of direct reading gauge. At gas pressures below this no other gauge is sufficiently sensitive to measure the pressure, and the ionization gauge showed inconsistencies. It was the investigation and elimination of these inconsistencies which lead to the development of ultra-high vacuum systems.

Limit of the Ionization Gauge

Until recently no pressure gauges existed which were capable of measuring gas pressures of less than 10^{-7} mm Hg, but indications that such pressures were attainable in special circumstances had been obtained from several indirect experiments. For example, it is known that the absorption of gas on a metal surface alters the ease with which it is possible to extract an electron from the surface, *i.e.*, alters the work function of the metal surface. The rate of absorption of gas on to the surface depends on the gas pressure, and thus the rate of change of work function of a surface freshly prepared in a vacuum, depends on the residual gas pressure, and may be used as an indication of that pressure. Experiments[1,2] on the work function and other surface properties carried out from about 1935 to 1940, indicated that when special precautions were taken, residual gas pressures less than 10^{-7} mm Hg could be obtained. When an ionization gauge was used in such a system, however, it showed a pressure higher than that obtained by the other, indirect methods.

These experiments indicated that in an ionization gauge there is a general background current to the collector which sets a lower limit to the pressure which can be measured by the gauge. The reading of the gauge becomes significant only when the pressure is sufficiently large ($> 10^{-7}$ mm Hg) to give rise to a positive ion current to the collector considerably greater than the background current.

An explanation of this behaviour was put forward by W. B. NOTTINGHAM (see ref. 4), who suggested that electrons from the cathode of an ionization gauge gain sufficient energy, in travelling to the anode, to cause emission of soft x-rays when they collide with the anode. The x-rays produced at the anode travel out in all directions, and some hit the collector where they liberate electrons. These electrons are drawn from the collector to the anode by the electric field, so that the effect of the x-rays is to give rise to a current of negatively charged electrons
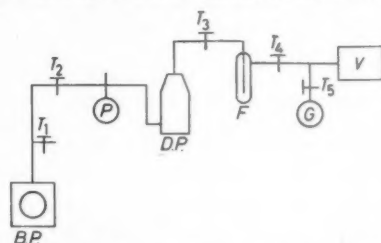

Figure 2. High vacuum system—B.P. is the backing pump, D.P. is the diffusion pump, T_1 to T_5 are vacuum taps, P is a drying agent to prevent water vapour entering the backing pump, F a cold trap to prevent vapour from the diffusion pump entering the vessel V to be evacuated, and G is a pressure gauge

away from the collector. This current is independent of the pressure, and, as far as the external measuring apparatus is concerned, is equivalent to a current of positively charged positive ions to the collector. The existence of such a current would

explain the discrepancies between the measurements of very low gas pressures by ionization gauges and by other means.

In order to test the hypothesis, R. T. BAYARD and D. ALPERT[3] designed an ionization gauge in which the electrodes were arranged as in *Figure 3b*. The advantage of this arrangement over that usually used (*Figure 3a*) is that the area of the collector is reduced by a factor of about one thousand. Thus if the x-ray hypothesis is correct, the background current should be reduced by the same factor, because although the x-rays are still produced when the electrons hit the anode, not as many of these are intercepted by the collector on account of its smaller area, and consequently not as many electrons will be liberated from the collector. Experiment showed that the lower limit of the gauge was reduced to about 10^{-10} mm Hg or less by this means, thus confirming the hypothesis.

This newly designed ionization gauge forms the basis of the new ultra-high vacuum systems[4]. In addition to being able to use the gauge to measure very low gas pressures, it was found in the experiments described above, that use could also be made of an effect which had long been known, and often regarded as a nuisance, namely, that the ionization gauge reduces the pressure which it is being used to measure. In fact, the gauge behaves as a pump.
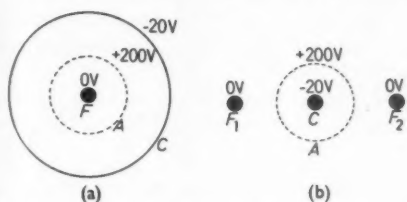

Figure 3. Cross section of an ionization gauge—(a) conventional arrangement of electrodes; F is the filament, A is the anode and C the collector; (b) Bayard and Alpert's arrangement of electrodes[3]; F_1 and F_2 are filaments, A is the anode and C the collector

The Ionization Gauge as a Pump

There are two processes occurring in an ionization gauge which remove gas from the vessel and cause the gauge to act as a pump. First, the presence of the hot filament of the gauge causes some molecular gases to split into their constituent atoms, and gases such as hydrogen, oxygen and chlorine are much more chemically active when in the atomic form, so that they are readily adsorbed by the surfaces of the gauge with which they come into contact. Second, the electrons from the cathode in their passage to the anode ionize gas molecules whatever the gas,

and the positive ions so formed are drawn to any surface, such as the collector, which is negatively charged; there the positive ions are neutralized by taking up an electron and adsorbed as neutral molecules of gas.
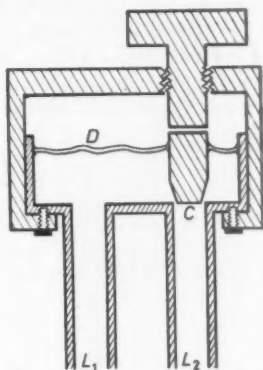

Figure 4. Schematic diagram of an all-metal greaseless ultra-high vacuum tap[4]—C is a tapered metal cone, D a flexible diaphragm, L_1 and L_2 are leads to the system

Both theoretical calculations and experiment show that the rate at which these processes occur is appreciable, but the usefulness of the ionization gauge as a pump depends on the degree of evacuation of the system before the gauge is switched on. The reason for this is that the surfaces of the gauge can not continue to adsorb gas indefinitely; they become saturated and the time taken to reach saturation depends on the pressure. For example, at a pressure of 10^{-4} mm Hg saturation for a normal gauge occurs in about one hour, whereas at a pressure of 10^{-9} mm Hg the time taken to reach saturation is about three years. Thus it can be seen that the ionization gauge becomes a practical proposition as a pump only if very low pressures, about 10^{-7} mm Hg, are first obtained by the other means.

It is also clear that if a lasting ultra-high vacuum is to be obtained the ionization pump must not be connected to a continuous source of vapour such as the oil in a diffusion pump or grease in a tap. A source of vapour of this sort continues to supply vapour until the pump is saturated even though the vapour pressure may be only 10^{-6} mm Hg or less. To isolate the ionization pump from all greases and vapours a greaseless tap was developed in the above experiments[4]. This tap, which is shown diagrammatically in *Figure 4*, is composed entirely of metal parts which are first degassed in a vacuum and then sealed together in an atmosphere of hydrogen to ensure absolute cleanliness. In operation, the tapered metal

D

cone C which is attached to the flexible diaphragm D is forced into the vacuum lead L, by means of the external screw arrangement. This external screw can easily be removed so that the valve can be heated when the system is de-gassed. It is found that a total thrust of one to two tons on C ensures a completely effective seal between the two parts of the system joined to the leads L_1 and L_2, without using grease.

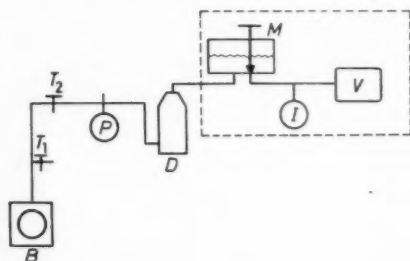Using this type of tap and an ionization gauge, an ultra-high vacuum system is readily assembled.

Figure 5. Ultra-high vacuum system—B is the backing pump, D the diffusion pump, T_1 and T_2 are vacuum taps, M is an all-metal greaseless tap to isolate both the vessel V to be evacuated and the ionization pump and gauge I

Ultra-High Vacuum Systems and their Applications

The complete system necessary to obtain a residual gas pressure about 10^{-10} mm Hg in a vessel V is shown schematically in *Figure 5*. In operation, the whole system is pumped out with the backing pump B and diffusion pump D using the same procedure as that adopted in a high-vacuum system. The section of the system shown enclosed in the dotted lines with the external screw of the metal tap M removed, is thoroughly de-gassed by enclosing it in an oven at a temperature of about 400°C for many hours. The special all metal, greaseless tap M is then closed and the ionization pump switched on. The ionization pump is used also to measure the residual gas pressure which is found to decrease from about 10^{-7} mm Hg—the value obtained with the backing and diffusion pumps—to about 10^{-10} mm Hg in about an hour, and to remain at this value as long as the pump is operated.

The ability to obtain such very low residual gas pressures readily in this way is an important advance in high vacuum technique, and opens up many new possibilities in fields of study such as the physics and physical chemistry of surfaces, where the presence of very small quantities of gas may have consequences out of all proportions to their concentration.

The new technique will, for example, find very great application in the fields of ionization physics and gaseous electronics in which the fundamental ionization phenomena occurring at surfaces and in gases are studied, and applied to devices as widely diverse as gas filled valves, electrical discharge lamps, switches, field emission microscopes, and ZETA, to mention only a few. It is well known that the processes of ionization occurring in a gas are markedly dependent on the purity of the gas, while those occurring at a surface depend greatly on the state of that surface[5]. Any improvement in the degree of evacuation obtainable in a system is therefore of great importance, because the lower the residual gas pressure the lower the impurity content when a gas is admitted, and the slower the rate at which any surface exposed to the residual gas is contaminated by an absorbed gas layer, which alters its physical properties.

The techniques are by no means confined to these fields alone, however, as may readily be seen from consideration of the results of an investigation which was made to ascertain the cause of very small rises in pressure which always seemed to occur in ultra-high vacuum systems, however carefully constructed and used[6]. In the course of this investigation methods were developed for measuring the vapour pressure and heat of vaporization of metals such as tungsten, and the rate of diffusion of gases through glass; these are important physical quantities which are very difficult to determine without the use of ultra-high vacuum techniques.

As a result of the investigation it was shown that the leakage into the system was due to helium, which is present only as a few parts per million in air, actually passing through the glass walls of the systems. An indication of the sensitivity of the system is given by the fact that the rate of leak which was detected was such that if it continued for a century it would give a pressure inside the system of one thousandth of a millimetre of mercury !

It is clear that the new ultra-high vacuum systems provide a powerful tool which will be increasingly used over a wide field of fundamental physical investigations and in their applications.

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The 1959 Waverley Gold Medal Essay Competition

RESEARCH is this year sponsoring The Waverley Gold Medal Essay Competition for the seventh year in succession. The Competition is designed to encourage the scientist in the laboratory and the engineer in the production plant to express his views and translate his work into an essay that will readily be understood by other scientists, directors of industrial firms and others interested in science and technology.

The **Waverley Gold Medal,** named after and bearing the coat of arms of the late Lord Waverley, together with **£100** will be awarded for the best essay of about 3,000 words describing a new scientific project or practical development giving an outline of the scientific–background, the experimental results and the potential application of the project or process in industry. The essays will be judged for technical content by specialists in the subject, for clarity of presentation and for style.

A second prize of **£50** will be awarded and also a special prize of **£50** for the best entry from a competitor under the age of thirty on 31st July 1959. If the first prize is awarded to a competitior under the age of thirty, the special prize will go to the next best entry. For full details write to the Editor of RESEARCH, 4/5 Bell Yard, London, W.C.2.

All entries must be received by the Editor not later than 31st July 1959

SCIENCE AND MALTING

A. H. COOK and J. R. A. POLLOCK

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In malting barley grain, complex changes occur which involve on the one hand the growth of the embryonic plant and on the other the degradation and partial assimilation of the reserves of the endosperm. Study of these processes is leading to improved methods of controlling both the yield and quality of malt.

FOLLOWING the germination of cereal seeds, growth over the first few days is associated with a degradation of the cell walls of the endosperm and with an intensive formation of enzymes; as a result some of the protein and starch originally present are broken down to simpler substances. The dried germinated grain is more friable than the original seed with the result that, by crushing, its contents are readily reduced to a powder, while the outer coverings of the grain remain as large fragments.

Infusion of the crushed meal or grist with hot water, as in the process of mashing in the brewery, then leads to substantially complete dissolution of the starch by enzymic action and so to the production of a fermentable solution. These changes are the basis of the malting and brewing processes, the final solution or wort being subsequently treated with hops and fermented to provide beer.

Barley and Malting

Malt is and has been for very many years made from numerous cereals in commercial quantities[1,2] but by far the most widely used grain for malting at the present day is barley. The historical reasons for this choice are obscure but they are probably connected with the fact that malt made from barley gives a higher yield of sugars than that from oats, while wheat is more suitable for bread-making than is barley.

The structure of the grain of barley (shown in *Figure 1*) is, moreover, especially favourable to its use for malting for the following reason. A small living embryo and a large almost inert endosperm are in close physical contact and are surrounded by two thin skins, the testa and the pericarp, which are themselves enveloped by a closely adherent husk. The latter, although it provides no useful material and therefore reduces the quantity of extract obtainable from a given weight of grain as compared with that potentially available in husk-free grain, is nevertheless beneficial. Thus in the malting of wheat, which is free from husk, the growing shoot tends to be easily broken off during the handling

of the grain and such damage may lead to unevenness in the development of the malt as a whole. In barley, on the other hand, the growing embryo is protected by the husk which also serves to prevent penetration by moulds.

In considering the types of barley most suitable for the maltster, several factors have to be taken into account. For instance, a primary aim of malting and also of mashing is to secure a large yield of fermentable sugar in the wort, a fact which incidentally implies that a barley rich in starch and therefore correspondingly poor in protein content is desirable[3]. Again, as the husks make no contribution to the extract and as in any one variety the relative weight of husk decreases with rise in grain-size, large corns are to be preferred. Further, the starchy endosperm should be of a mealy rather than of a vitreous appearance as experience has shown that mealy corns are malted more easily. By employing such criteria to segregate desirable barleys, remarkable progress has been made in improving quality with regard to malting characteristics as well as to yield and other agricultural factors.

Since the beginning of the present century, selection and hybridization have been widely used in Europe with the result that several varieties of two-rowed spring barley (*Figure 2a*) are now available which represent very considerable advances on the strains earlier in use[4]. Thus Proctor, a hybrid between the Scandinavian Kenia and the British Plumage-Archer, combines desirable features of both parents to such an extent that it outyields each by 15 to 20 per cent or more, while malts made from it are of excellent quality. Emphasis has been laid, with similar success, on six-rowed barley (*Figure 2b*) in the United States and Canada[5], this type being preferred where the crop has to prove adaptable to a wide range of climatic conditions. Parallel with these varietal improvements, there has been a growing appreciation of how treatments with manure may affect yield and malting quality. Thus it has been shown that, during the early stages of growth,

nitrogenous fertilizers have the effect of increasing the number of tillers, or grain-bearing stems, per plant and hence the yield of barley per acre. The presence of these same fertilizers at later stages has much less effect on yield, although it substantially increases the protein content of the crop, as is desirable in barley grown for feeding purposes[6].

The Malting Process

The first stage in the conversion of barley into malt involves introducing into the grain sufficient moisture to induce germination and to facilitate the diffusion throughout the grain both of enzymes and of the products of their action. It is generally found best to aim at a moisture content of 42 to 45 per cent. In normal malting practice, barley, in batches often of 30 tons in weight, is steeped for 36 to 72 hours.

The next stage, during which the barley is allowed to germinate, is carried out in one of three distinct ways. In the traditional method of floor-malting, still largely used in the United Kingdom, the moist grain is spread on a floor and, as growth proceeds, is turned from time to time either by hand or by mechanical means. The temperature of the bed is controlled by adjusting its thickness, an operation which calls for great skill in judging the condition of the grain. In one of the other systems the steeped grain is placed in a drum which is rotated intermittently while air of controlled temperature and humidity is introduced. Similar aeration is practised in the third method, the characteristic feature of which is that the soaked grain is allowed to germinate in deep layers in boxes, called Saladin boxes fitted with suitable mechanical devices for turning the boxes as required.
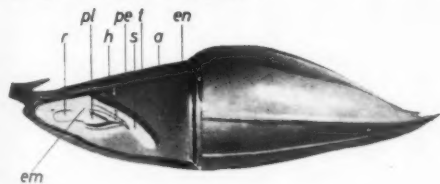

Figure 1. Structure of the barley corn—a, aleurone layer; em, embryo; en, endosperm; h, husk; pe, pericarp; pl, plumule; r, rootlet; s, scutellum; t, testa

Carbohydrate Degradation

During the earliest stages of germination the embryo respires at the expense of its own sugars, sucrose and raffinose[7], which naturally soon become exhausted so that further development involves depletion of the reserves contained in the endosperm. These reserves are mobilized by enzymes secreted by the embryo through its scutellum[8], a shield-like structure in contact with the endosperm (see Figure 1). The proteinaceous cells of the aleurone layer which

Figure 2. Ears of (a) two-rowed and (b) six-rowed barleys. Two oppositely placed rows of grain occur in the two-rowed barley (a) while in (b) six rows in all are present

surrounds the starchy inner endosperm also play a minor part in liberating enzymes into the body of the grain[9,10]. The whole sequence of change is, as already stated, initiated by the enzymic degradation of the cell walls which, though probably never complete in ordinary malting[11,12], nevertheless proceeds far enough to make the walls readily permeable to other enzymes such as the amylases and those concerned in the hydrolysis of proteins. The changes taking place in the cell walls are related to the hydrolysis of pentose-containing polymers[13] as well as to the degradation of insoluble hemi-celluloses containing glucose[14].

Though little detailed progress has yet been made in elucidating the changes which take place in the insoluble hemi celluloses, some of the products must be similar to, or identical with, the water-soluble gums which are themselves substantially degraded during malting. These gums and their enzymic cleavage have

been studied intensively by I. A. PREECE and his collaborators[15] and by W. O. S. MEREDITH[16], while the structure of the chief components, β-glucan[17], has been shown[18] to be similar to that of lichenin[19] in comprising an unbranched chain of glucose units linked by α-1:3 and α-1:4 linkages in equal numbers.

As a result of this cytolysis, the starch granules of the endosperm are brought within the sphere of action of the enzymes secreted by the embryo. Part of the starch is thereby degraded to provide free sugars accounting for some seven to ten per cent of the weight of the grain. By examining, with the aid of

chromatographic methods, the gradual production of these sugars[20],[21] an almost complete balance sheet for hexose units during malting has been constructed[22] and this reveals that there is a pronounced synthesis of fructose derivatives during the process. In some cases this synthesis, which largely involves the formation of sucrose (*Figure 3*), goes on even when the grain is being heated in a current of air in the kilning stage, the last of the processes of malting. The precise mechanism by which this formation of fructose units occurs is at present unknown but it evidently takes place at the expense of glucose units.
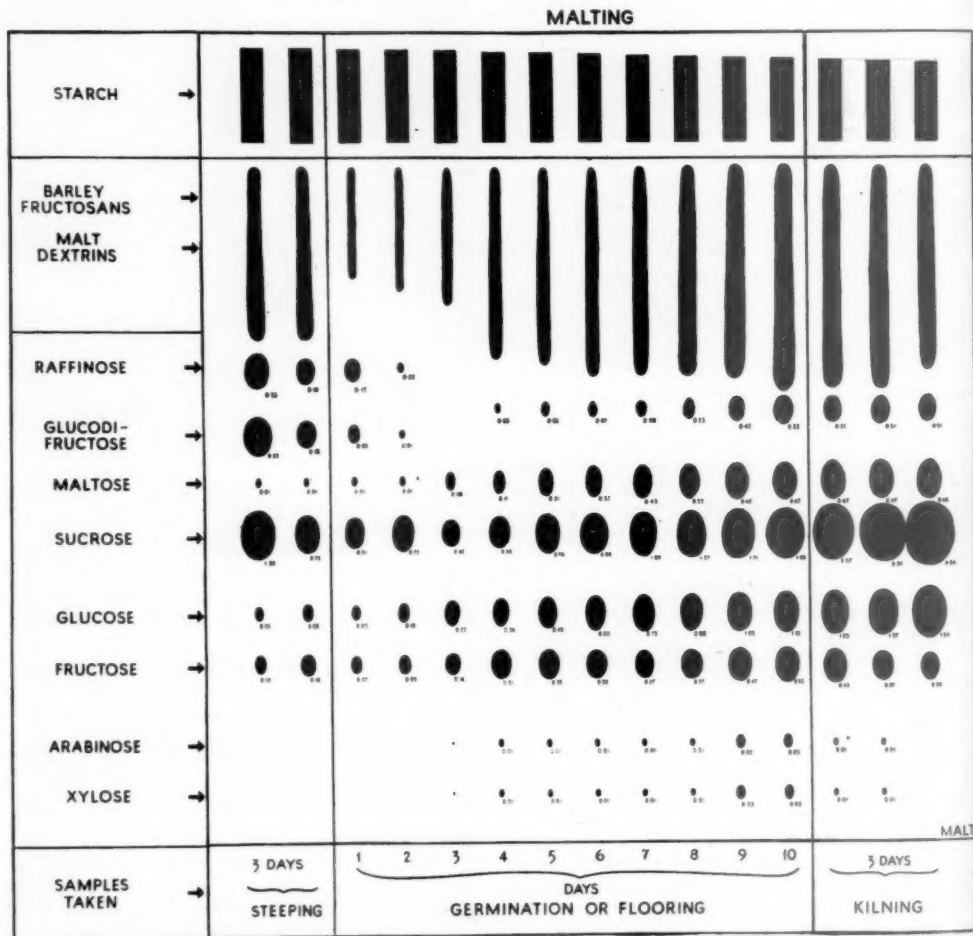
MALTING

Figure 3. Variations in concentration of carbohydrates of barley during malting. Individual components are shown as spots on a paper chromatogram, the area of each spot is proportional to the quantity of the sugar concerned

Protein Degradation

The parallel degradation of proteins in the endosperm involves largely both the alcohol-soluble prolamine hordein and the alkali-soluble glutelin. Of the former, about two-thirds is commonly solubilized while about half of the latter originally present may be broken down[23]. Though the total quantities of albumins and globulins undergo little change during malting, this probably indicates the existence of a dynamic equilibrium rather than a static condition, for many of the enzymes formed during malting are found among these groups of proteins.

In general the syntheses of most enzymes during growth follow roughly parallel courses (see, for example, *Figure 4*) but the occurrence of β-amylase in barley both in the free state and in an insoluble condition has led to the suggestion that the effect of malting is limited in this particular to a solubilization of the ' bound ' form of the enzyme. Recent work has, however, shown that this is not the case for, during steeping, the quantities both of free and of the latent enzyme decrease rapidly almost to vanishing point whereas, during germination, synthesis of the free form only supervenes[24].

All the above changes depend on the vital activity of the embryo and the quality of the malt thus depends on the uniform germination of the constituent corns of the piece of barley being malted. In this connection dormancy, a phenomenon which prevents rapid initiation of germination, poses important problems particularly when it is most pronounced during the period immediately after harvesting[25,26]. The difficulties generally disappear in about six weeks but even after this period some barleys and especially those grown in cold wet seasons, such as are often met with in Britain, still fail to germinate uniformly under normal malting conditions. Recent investigations have shown that when this is the case the grain can be induced to germinate satisfactorily only if the steeping process is strictly controlled[27], for the degree of germination of such barley falls sharply when either more or less than a certain quantity of water is present[28]. The term ' water-sensitivity ' has been suggested to describe this behaviour (*Figure 5*).

Malting Loss

While uniform germination and some degree of growth appear to be essential to the production of good malt, another factor which must be taken into account is the malting loss occasioned by both the growth of the rootlets (which are removed after kilning) and the respiration of the developing embryo[29]. The loss amounts normally to some ten per cent of the weight of the grain. Clearly, the further growth proceeds, the greater will this loss be and the malster aims, thus, to strike a satisfactory balance between the yield of malt obtained and the adequate development of enzymic activity.
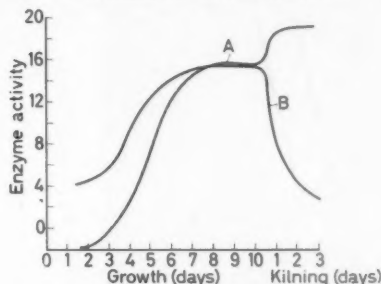

Figure 4. Course of variation in the activities of α-(*curve* A) *and* β-amylase (*curve* B) *during germination and kilning*[37]

The respiration of the embryo during malting depends largely on the activity of cytochrome oxidase[30] and a considerable amount of knowledge is now available on the glycolytic pathways and general respiratory mechanisms of the embryo[31]. In general, these parallel those of yeast. Several investigations have been concerned with whether the ordinary level of malting loss is essential and it has been shown that analytically satisfactory malts can be obtained with material from which the embryos have been removed after only three days' growth, following which the endosperm is left to autolyse partially[32], or by treating the grain with phosphates[33], potassium bromate[34], or coumarin[35]. There is thus good reason to hope that in the near future malting loss will regularly be reduced to much lower levels than hitherto.

Kilning Conditions

The germinated grain, in which softening of the endosperm cell walls is substantially complete and in which about two-fifths of the protein is degraded to peptides and aminoacids, is in commercial practice then conveyed to a kiln in which it is slowly dried in a stream of hot air. During kilning, the life of the grain is brought to an end while at the same time its moisture content falls from about 42 per cent to 4 per cent or less. The dry malt obtained is similar in appearance to the original barley but is crisper and more pleasantly flavoured.

The conditions used in kilning have a pronounced effect on various properties of the malt and hence on those of the derived beer. For instance, if the malt becomes warm while still very moist an intense enzymic activity ensues with concomitant formation of comparatively large quantities of simple

sugars and aminoacids.   At temperatures over
100°C these substances interact to give the character-
istic flavour and pigments of dark malts[36].   Con-
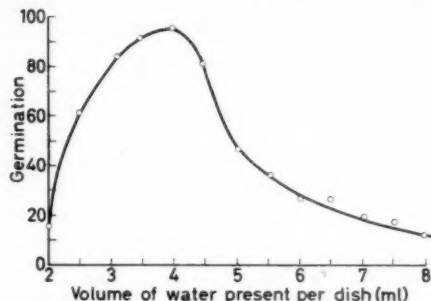versely, if most of the water is quickly removed at a

Figure 5.   Response of water-sensitive barley
to graded increases in the amount of water
present during germination

relatively low temperature, sugar and aminoacid
formation is minimized and the enzyme content of
the malt is better conserved.   This latter treatment
afford malts particularly suitable for the brewing of
pale beers.   A far reaching effect of the tempera-
ture of kilning is concerned with regulating the ratio
of the two main starch-splitting enzymes, α- and
β-amylase, of which the latter is easily inactivated
by heat (*Figure 4*).   A preferential destruction
of β-amylase affects the composition of wort as
α-amylase acting alone on starch gives a wort
containing a large amount of non-fermentable
carbohydrates.   For this reason, regularity in wort
fermentability depends markedly on kilning pro-
cedures.

Conclusion

Scientific examination of the age old traditional
process of malting has thrown into relief some of
the major changes which occur.   Future develop-
ments in connection with the scientific aspects of
malting are likely to help elucidate the nature of
the structural components of the cell walls as well
as the structure of the reserve proteins and how
they are degraded.   Much, however, remains to be
investigated with regard to the interconversions of
the various sugars during malting and the detailed
mechanisms of growth and of respiration.

Considerable economic advantages could arise
from the development of methods of controlling
growth and respiration while a knowledge of how
the enzymes are synthesized in the grain during
malting would be of very great practical value in
maintaining the quality of the final malt.

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GOLDEN JUBILEE

of the Indian Institute of Science

V. S. SWAMINATHAN

J. N. TATA (1839–1904)
Founder of the Indian Institute of Science, Bangalore

THE Indian Institute of Science, which was the first institute in India founded for the specific purpose of furthering advanced research work in pure and applied sciences, celebrated its golden jubilee in February 1959. President PRASAD inaugurated the ceremony on 2nd February, 1959, before a distinguished gathering of scientists from all parts of the world, including H.R.H. The Duke of Edinburgh representing the British Association for the Advancement of Science.

What Henry Ford and Rockefeller were to America and Nuffield to Britain, JAMSETJI NUSSERWANJI TATA was to India. Of the three great schemes with which Tata's name is linked, namely, the founding of the Indian Institute of Science, the harnessing of hydroelectric power in Western India and the establishment of a modern iron and steel industry, the first is perhaps the most important. As early as 1889 Tata conceived the idea of setting up a research centre for the promotion of the material and industrial progress of India but he did not live to see the fruition of his ideas, and it was left to his sons, with government aid, to carry on the work. In 1906, Dr M. W. TRAVERS was appointed the first director of the Institute and the first students were admitted about five years later. In those early years the Institute was concerned only with pure and applied chemistry and engineering technology but today it is responsible for research and training in many other branches of science, the social sciences and engineering.

Chemical and Biochemical Research

At the present time the department of general chemistry is conducting research on the synthesis of amines using ammonia and alcohols as starting materials; the adsorption of gases by industrial catalysts; chromatographic and polarographic analysis and the standardization of non-poisonous electroplating bath compositions. Other research work ranges from investigation of molecular structure and dipole moments to the beneficiation of sulphide ores found in Mysore. The department has contributed to the success of several industrial undertakings in the Mysore State: factories are now producing dichromate, porcelain, soap and sandal oil. Organic chemistry research has always been concerned with essential and fatty oils, natural and synthetic drugs and turpenes. Recently investigations on the carbohydrates and the synthesis of naturally occurring steroids have been carried out and the beginning of the domestic oil hydrogenation industry can be traced to this pioneer work. (Several of the projects have been sponsored by the Council of Scientific and Industrial Research.)

The biochemical department has facilities for tackling fundamental problems pertaining to enzyme chemistry, vitamins, antibiotics, food and nutrition and cytogenetics. It has developed a multi-purpose food from the groundnut and sesame oil seedcake which provides cheap and nutritious food for the poorer people and it has sponsored the use of groundnuts enriched with vitamin B.

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Research in Physical and Engineering Sciences

The physics department has specialized in various aspects of crystal physics. It is equipped for investigations on light scattering, Raman and infra-red spectroscopy, x-ray analysis, and the physical properties of crystals. Special precision techniques have been evolved for light scattering experiments and for Raman spectroscopy in the ultra-violet region. In addition, a number of short-term projects have been sponsored, as for example one on electronic computers.

A special department equipped with six wind tunnels of various types and sizes and a structures laboratory in which the stress analysis of structural elements can be made carries out research on diverse problems pertaining to aerodynamics and elasticity; it investigates, for example, the behaviour of swept-back wings and tests aeroplane models. Fundamental work on boundary layers, turbulence phenomenon and the drag of bodies moving at supersonic speeds is being carried out not only for its scientific value but also for application to the design of various types of aircraft components. This department has the advantage of working in close liaison with the Hindustan aircraft factory in Bangalore.

The internal combustion engineering department was set up in 1945 to provide facilities for training students in the theory, design and manufacture of such engines, and for research and assistance to the industry. Engine testing facilities have been developed to cover a range from 5 h.p. to 1500 h.p. and speeds from 500 to 5000 rev/min. A laboratory for studying fuels and lubricants is a recent addition. Also, facilities are available for testing large compressors, gas turbines (up to 1000 h.p.) and combustion chambers. Several items of work sponsored by the Council of Scientific and Industrial Research and the Atomic Energy Commission have been undertaken.

The research programmes of the metallurgy department are designed to fit into the expanding industrial pattern of the country: the production of nuclear grade zirconium, electroplating from fluoborate baths, aluminium and its alloys and the effect of silver on the recrystallization temperature of copper. Studies on the electrical conductivity of aluminium have shown that commercial grade Indian metal is markedly improved by adding either boron or calcium to it in small but controlled quantities.

As early as 1911 an electrical technology department was established primarily to train engineers and twelve years later it was extended to include electrical communication engineering. The present department was formed in 1947, with the heavy engineering part of the old electrical technology department as the nucleus, and the electrical communication section was made into a separate department. The engineering department is now organized in four sections: electrical, high voltage, civil and hydraulic, and mechanical. Research on problems linked with power system design and operation, electrical machines, illumination, *etc*, is carried out. Every important power system in India has been studied on its a.c. network analyser (see *Figure 2*) in order to predict the actual operating conditions, and test the stability under fault conditions. Among the main contributions of this section are the universal metering testing equipment with a special phase shifting device for testing at different power factors, and the transformer analogue computer developed for studying special engineering problems.

The mechanical engineering section trains graduate engineers in the design, operation and maintenance of thermal power stations. Standard theoretical instruction is given and the department contains a modern 600 kW steam plant for practical field training. Research is mainly on transfer processes, dynamics of materials and machines, foundry and instrument technology.

The civil and hydraulics section runs a two-year post-graduate course in civil power engineering. The department aids industry by testing the efficiencies of pumps and the quality of materials used in construction. The designs of the earthen flanks of the high dams proposed for the hydroelectric project at Coorg and other places were prepared after soil studies had been carried out here.

The high voltage engineering laboratory trains personnel in the appropriate techniques, it undertakes research programmes on behalf of industry, standardizes high voltage measurements and tests electrical equipment at high voltages. Its main equipment comprises a 3MV, 50 kW impulse generator; a 200,000 amp, 30 kW impulse current generator and three testing transformers, each of 50 cycles and 1000 kVA. Some of its current activities pertain to development work on electrical porcelain based on indigenous raw materials.

The department dealing with electrical communication engineering organizes post-graduate courses in electronic, microwave, line communication and acoustical engineering. Current research includes microwaves, radio wave propagation, analogue computation, *etc*. The analogue computer (PREDA), set up by Professor V. C. RIDEOUT, has been busy solving a number of mathematical problems for several departments of the Institute.
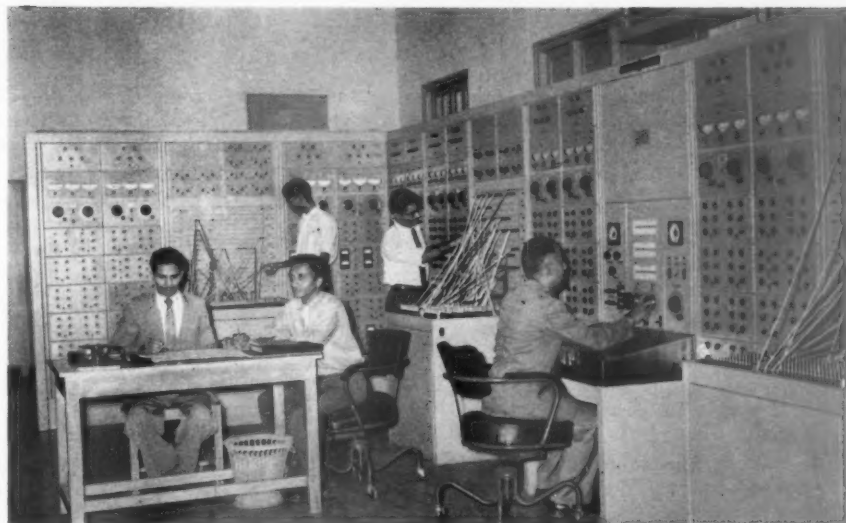
Figure 2. An a.c. network analyser in the Electrical Engineering Department, Indian Institute of Science, Bangalore

Other Research Activities

In the chemical technology and engineering department facilities are available for research on fuel technology, ore treatment and the separation of isotopes. The treatment of low ranking local coals, cracking and aromatization of hydrocarbons and hydrocarbon synthesis under normal and under high pressures is being investigated. Work on mineral treatment is directed mainly towards the economic use of low-grade raw material like graphite, and evolving new processes for the manufacture of iron and steel. The enrichment of heavy water from bitterns, the enrichment of uranium 235 from salts by adsorption and boron 10 enrichment by thermal diffusion methods are being studied with particular interest at the present time.

The activities of the pharmacology laboratory are naturally concerned with the elucidation of malarial and tubercular problems, and on investigation of the medical properties of local plant products empirically used in the indigenous Ayurvedic system of medicine. Metabolism of the tubercle bacteria, the mechanism of drug resistance and the development of new drugs, both synthetic and natural, receive priority. For a complete cure of malaria and other bacterial, protozoal and viral infections, besides the specific drug therapy it is essential to build up the hosts' resistance. To this end changes in the various constituents of blood and tissues and the influence of the vitamins and various anti-metabolites in malarial infection have been studied to understand the host–parasite relationship. This laboratory assists the Indian pharmaceutical industry by carrying out biochemical assays of their products, and the state governments by acting as a standards testing laboratory for some of their pharmaceutical purchases. The fermentation technology laboratory is interested in industrial fermentations and in microbial and insect nutrition. It has made useful contributions to the techniques used for obtaining high yields of alcohol and antibiotics like penicillin and streptomycin. Also, the problem of increasing the yield of silk by improving the nutrition of the silkworm has been investigated with marked success.

Other departments, which cannot be mentioned here in detail, include applied mathematics and the economics of social sciences section. The library of the Institute is probably the best of its kind in India and it now possesses some 50,000 volumes and receives over 1000 periodicals each year; it caters for the needs of the Indian National Scientific Documentation Centre at New Delhi. The present annual expenditure of the whole Institute is about £52,000. It has trained nearly 3000 post-graduate students since 1911 and many of these hold positions of responsibility in government departments, industry and at the universities. The Institute has in fact contributed significantly to the steady scientific and industrial progress in India.

SURVEY

A History of Technology

Where does history end and the present begin? The editors of *A History of Technology* have decided that it ends* at the beginning of the twentieth century coinciding with the advent of air transport, the telephone and heavy electrical industry. This date seems somewhat arbitrary for the final volume therefore does not mention nuclear energy, plastics or synthetic fibres. This is a serious omission for their development has changed the whole course of modern industry and indeed I.C.I. Limited, whose financial support has made the preparation of these five volumes possible, is one of the largest producers of both plastics and synthetic fibres in the United Kingdom.

The fifth volume of *The History*, published recently, deals with the growth of technology in the late nineteenth century. It is well written and produced and apart from being a work of reference it will be a joy to inquisitive boys and their parents. The subjects range from food production and preservation to the metals industry, the growth of the petroleum industry, engines, the generation and distribution of electricity, the growth of the chemical and transport industries, civil engineering, the making of machine tools, the textile industry (see for example *Figure 1*), and the production of rubber. It would I am sure give the reader even more pleasure to glance at these volumes in future years if they were supplemented by at least one other tracing the technological development from the year 1900 to the building of the world's first atomic power station.

Increasing the Speed of Computers

A tiny magnetic device which will increase the ' thinking ' speed of electronic digital computors—and of missile guidance systems—by factor of about 10 or 12 has been developed by the Research Laboratories of the National Cash Register Company in the United States. The device is a pin-sized glass rod, about 0·015 in. in length covered with a magnetic coating. The coating appears to be applied over a layer of conducting material by ' a special electrochemical process ' developed in these laboratories. Two small coils of wire around the rod convey the information to be stored or read out and only 0·02 W of power is required to store up each bit of information.

It is claimed that information can be recorded or released at speeds of 25 to 250 microseconds and that this type of memory store can operate efficiently at temperatures up to 150°C.

Better Communications

To meet the increased demand for inter-continental communications, the General Post Office has devoted a large proportion of its research and development facilities—and of course its capital investment—to the modernization of the telephone and telegraph services. The first transatlantic telephone cable has now been in use for over two years and is a success both from the commercial and the engineering points of view. It is now proposed to double the number of conversations which can be carried by the cable at any one time, since telephones are arranged so that only one person can speak at any one instant and the return channel is therefore idle for at least half the time. By installing a system of fast electronic switching to connect the appropriate receivers and line at each end, a single channel can be used both for the outward and the return conversation.

It is unlikely that the demand for fast communication will be satisfied by either this or the other proposed cable links and therefore modernization of radio telephone and radio telegraphy equipment will be undertaken over the next few years. A start has already been made at the Ongar radio station, where seven new transmitters† came into operation at 11.30 a.m. on Thursday, February 19th; the first message was sent by Lord Chesham to the Royal Yacht *Brittania* somewhere off Singapore and, in spite of bad communications in the Singapore area, the reply was received in about two hours.

The Ongar radio station is the principal telegraphy station run by the Post Office. It receives messages by land line from the head office in London and, in the new equipment, these are first converted to the standard frequency of 3·1 Mc/s and delivered to the transmitter proper at a standard power level of 0·25 W. The signals are sent out on any one of six pre-selected frequencies ranging from 4 to 27·5 Mc/s. (Each of the new transmitters radiates a peak power of 30 kW.) The frequency can be selected, changed or the transmitter shut down completely in a matter of seconds by remote control.

† DS13D transmitters supplied by Standard Telephones and Cables Ltd
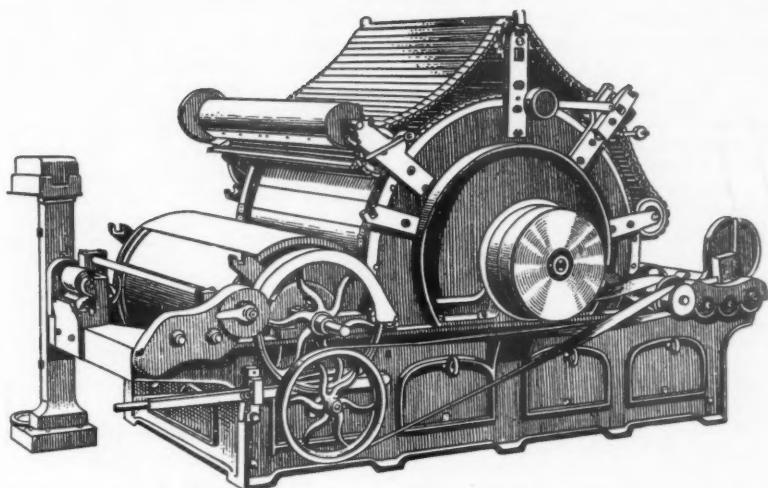
Figure 1. The revolving flat card was a standard machine in the cotton industry by about 1887. The cotton is carded between the surface of the continuous chain of revolving flats and the central cylinder below. The machines vastly improved the quality and nearly doubled the quantity produced. (*Reproduction from* A History of Technology, *Vol. 5*)

Each of the aerials at Ongar is directed and will only transmit to one particular part of the world but each can function over a wide range of frequencies. Frequencies have to be changed during different parts of the day, depending on ionospheric conditions, and usually at least two frequency changes per day for any one direction are required. Any of the transmitters can be connected to a suitable aerial, in some cases by remote control and in others manually. The station transmits by short wave to all parts of the world—this includes the transmission of pictures, the leasing of 40 international radio links to private customers such as press agencies, international air lines, shipping companies, *etc.* Long waves are still used for telegraphy to the Continent.

The main advantages of the new transmitters are ease and flexibility of operation; should the public demand change from telegrams to telephone conversations they could easily be converted to the latter.

Scientific Research in Schools

The first report, covering the year up to the end of June, 1958, has been issued by the Committee which was set up by the Royal Society to assist schoolmasters and schoolmistresses who wished to carry out scientific research in schools. About 57

requests for advice were received and twelve research projects were started with the assistance of the Committee; these twelve are in addition to the nine projects previously sponsored by Shell Research, Ltd.

The subjects chosen by the schools vary widely, ranging from the development of an electronic timing device, nitration and nitrosation by tetranitromethane, to selective breeding experiments. Fellows of the Royal Society review all the projects under consideration and many have agreed both to act as advisors and to lend equipment from their own laboratories.

Long Term Grants for Research

The D.S.I.R. has decided that money will in future be given to universities to enable them to undertake special researches for periods of as long as 17 years. These grants will be available for an initial period of three to seven years with the possibility of two renewals, each for a maximum of five years. A third renewal will not normally be given. This change in policy—previously the maximum was five years—has been made to enable universities to plan and carry out complex and more expensive researches. The first closing date for applications is 1st March, 1959.

BOOK REVIEWS

Progress in Semiconductors: Volume 3

(vii + 210 pp; 10 in. by 6¼in.)
London: Heywood. 55s

THIS third volume in a series which should now be well known to all research workers in the field of semiconductors fully maintains the high standard set by its predecessors. In such a rapidly advancing subject it is a practical impossibility for a review article to be completely up-to-date; but the seven articles presented here come as near to it as makes no matter.

The authors, editors and publishers are to be congratulated on the speed with which they must have done their work. Each article is of value not only to the active research worker in its own specialized field, but perhaps even more so to the worker in related fields, who has perhaps not had time to keep in close touch with the current literature. And possibly those who benefit most from these reviews are the many scientists and engineers in industry and elsewhere who are engaged in applying the results of pure research to practical development. In general such people have little time for personal detailed study of all the current scientific periodicals of interest to them. A timely review article—provided it is of the high standard exemplified here—is invaluable to them.

The subjects chosen for the present volume cover a wide field. ' The Magnetoresistivity of Germanium and Silicon' by M. GLICKSMAN and ' Scattering and Drift Mobility of Carriers in Germanium' by M. S. SODHA deal adequately with some fundamental properties of silicon and germanium which are of interest to many. ' Lifetime of Excess Carriers in Semiconductors' by A. MANY and R. BRAY is a very comprehensive review by two well known workers in this important subject. It may be recommended unreservedly as a standard source of reference.

' The Chemical Purification of Germanium and Silicon' by J. M. WILSON and ' Silicon Junction Diodes' by D. E. MASON and D. F. TAYLOR complete the five articles which deal with germanium and silicon. The former gives an insight into the chemical problems involved in extreme purification, and is particularly relevant to silicon. The latter deals with the subject of device design and fabrication. The remaining two articles deal with compound semiconductors. ' Electronic Conductivity of Silver Halide Crystals' by J. W. MITCHELL and ' Electronic Processes in Cadmium Sulphide' by J. LAMBE and C. C. KLICK both are concerned largely with photo-conductive processes.   J. T. KENDALL

Manual of Scientific Russian

T. F. MAGNER

(101 pp; 10¾ in. by 8 in.)
Minneapolis: Burgess Publishing Co.; London: Mayflower Publishing Co. 37s (paper covered)

THIS book is not a textbook for the learner, even if he is mature and used to complex structures, as is claimed by the author in the introduction. It cannot be used, as is implied, without the guidance of a teacher and the opportunity for exercise which can only be provided by ample, graded reading matter. On the other hand, Sections I to V, which form the main bulk of the book, are an *excellent*, clear and concise manual for revision and reference and for this purpose the format is very suitable. It contains a list of the Russian names of the elements and a useful bibliography of scientific dictionaries.

The collection of Russian texts appears totally inadequate, particularly as no English translations are given and the short section on translation techniques, though useful, is too limited to make up for this. The book in fact fails as a manual of *scientific* Russian, though it may be invaluable to a person with a fair knowledge of the language, when used in conjunction with well chosen texts and a good dictionary.   T.M.M.

Fluorocarbons

M. A. RUDNER

(viii + 238 pp; 7½ in. by 5 in.)
New York: Reinhold; London: Chapman and Hall. 46s

THIS little book is devoted to comprehensive accounts of two fluoro-polymers, polytetrafluoroethylene and polychlorotrifluoroethylene. It forms one of the Reinhold series of books dealing with plastics applications, which is intended to be useful to everyone concerned with the plastics industry, not only on the manufacturing and processing sides, but also all users and potential users of the materials. This particular book certainly succeeds in achieving its objective. It has 238 pages (ten chapters) devoted to the general properties, processing techniques, and applications of these two polymers. Their properties are unique, in particular their high temperature stability and resistance to chemical attack. They find wide specialist application in the electrical, mechanical, chemical, anti-adhesive and lubrication fields, and new uses are continually being developed. Their dollar sales volume in 1956 reached the surprising total of $80 million.

The types of polytetrafluoroethylene and polychlorotrifluoroethylene commercially available in the United States are described, together with a brief account of the chemical background of the materials. The essentials of the processing techniques for polytetrafluoroethylene, such as moulding, sintering, annealing, extrusion, etc, are given, and also the uses of aqueous dispersions of the polymer for film-casting and coating. Impregnations of porous structures, lining of pipes, and the uses of inorganic additives are also considered. The processing of the du Pont product, Teflon 100X, which can be melt-extruded, is described briefly. The processing techniques for polychlorotrifluoroethylene are dealt with similarly.

The uses to which components of these two polymers are put in the electrical field are many, particularly in insulation at high frequencies and high temperatures. Mechanical applications arise from the low coefficient

of friction of polytetrafluoroethylene, and the fact that very few materials will stick to it. They include self-lubricating bearings and the covering of surfaces of equipment for processing sticky materials. Many uses are found for these polymers in the chemical industry because of their chemical stability. Protective coatings for a wide range of objects and materials can be made from fluid dispersions. The author is enthusiastic about these polymers and forsees increasing uses for them.

The choice of title for the book is perhaps an unfortunate one since it rather suggests a chemical work, and anyway polychlorotrifluoroethylene is not a fluorocarbon. The book is intended primarily for engineers and plastics technologists. There is little chemistry in it, but many chemists and others will nevertheless find much useful information about the properties of materials which, as the author says, enter into more basic fields of endeavour than do any other resins.   J. C. TATLOW

The Universe

Edited by *Scientific American*

(142 pp; 7½ in. by 5 in.)
London: G. Bell & Sons. 13s 6d

THIS small book contains six sections written by experts, many from Great Britain, on how and why scientists and astronomers are investigating the universe—its history, the origin of the elements, the content and the evolution of the galaxies. The two prevailing cosmological theories, the steady-state and the evolutionary theory, are discussed and several articles describe how observations on very distant galaxies are made by measuring the ' red shift ', the distribution of the galaxies and the radio emission received from them. In spite of all these investigations the conclusions that can be deduced are still limited for the techniques which can be applied are limited. At present ' guesses ' still have to be made although these can be based on scientific facts.

There is at present, and perhaps always will be, a very great dearth of well written ' popular ' science books and thus a book of this type is very welcome. It will be of interest both to scientists, amateur astronomers and others interested in the progress of science and astronomy.
    E.S.

The Individual and the Universe

A. C. B. LOVELL

(111 pp; 7½ in. by 5 in.)
London: Oxford University Press. 10s 6d

The book contains the six B.B.C. Reith lectures broadcast by Professor Lovell during the autumn of 1958. (A shortened version of these lectures was presented on television.) Many will of course disagree with the views put forward by the author, but the book does nevertheless make stimulating reading.

LETTER TO THE EDITOR

A Paradox in Finish Turning

SIR,

It has been known for some time that tool wear adversely affects surface finish when fine turning steel[1,2], the main cause being groove formation under the trailing edge which occurs with both carbide and ceramic tools[3-5]. On the other hand, when turning with sharp tools, regenerative chatter introduced under certain conditions into the system tool/workpiece/machine has a similar effect[6,7]. The fundamental difference between those phenomena is that the first one causes the microgeometry within one feed mark to deteriorate, whereas the latter is connected with waviness*.

The interesting and practically important question which arises is the condition of surface finish when both phenomena are present, that is in prolonged turning of steel under vibratory conditions. In contradiction to what might have been expected, it appears from a number of experiments recently carried out by the author at the Wolverhampton and Staffordshire College of Technology, that a decrease of the roughness measured may occur, and in some cases this is appreciably below the value obtained when vibration is absent.

* The centre line average roughness h_{CLA} measured with a stylus instrument such as the Talysurf increases after only a few minutes of cutting, owing to concentrated wear, by a factor of two to six[5]. The increase under vibratory conditions with a sharp tool is usually within similar limits[6].

For example from a series of experiments, all of which showed similar qualitative trends, *Figure 1* shows two profiles obtained on a Talysurf Model 2 surface finish

(a) h_{CLA} = 90 µ in.

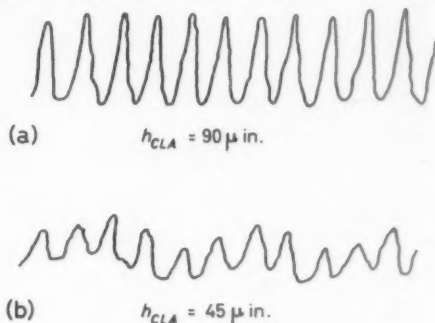
(b) h_{CLA} = 45 µ in.

Figure 1.   Profiles of a fine turned surface with a worn tool when vibration is (a) absent and (b) present

analyser after cutting for a total length of 8500 ft during fine finish turning of 0·38 per cent carbon steel with a carbide tool (tool nose radius $r = 0.018$ in., rake angle $\alpha = 0°$, cutting speed $v = 1300$ ft/min, tool feed $f = 0.002$ in/rev., depth of cut $t = 0.005$ in.). The profile in *Figure 1a*

was produced in an experiment without, and the profile in *1b* in an experiment with vibration. In spite of the pronounced waviness of *1b*—an increase of maximum roughness over ten feed marks by a factor of nearly two when compared with h_{max} within one feed mark—the decrease of h_{CLA} (0·1 in. cut-off length was used) in this particular case was nearly by 50 per cent. With the increased pitch of undulations these results might be false due to the lack of longer cut-off lengths than 0·1 in. on the instrument employed. However, in most of the experiments supporting this contribution, the tool feed was less than 0·004 in/rev and the pitch less than 0·1 in. An increase of waviness has also been observed with a trend towards a decrease of depth of individual feed marks, *i.e.*, a decrease in h_{max}.

An analysis of the microphotographs reproduced in *Figures 2* and *3* showing the clearance faces of the tools after the two experiments had been completed may throw more light upon this paradox. As shown previously[3-5], the difference of wear magnitudes B_1 (the length of the first groove) and B (the width of the wear land) is directly responsible for the surface finish generated; the groove length also depends on the complex phenomena occurring in the narrow boundary region of the interface between tool and workpiece[3]. However, under vibratory conditions this boundary region periodically moves along the trailing edge, thus causing localized wear to be spread over a wider area and this may be clearly seen when both microphotographs are compared. In consequence, although wear on the clearance face is more severe under

Figure 2. Clearance face of the worn tool after the completion of the experiment (a) in Figure 1 (reproduced two-thirds of original size)

vibratory conditions, approximately 20 per cent in the present case, the difference $(B_1—B)$ in *Figure 3* is less than in *Figure 2*. This favourable influence upon the depth of individual feed marks is still increased by less secondary cutting between the grooves, because, owing to a widening of the grooves, the cutting edge becomes straighter.

The above results make it possible to conclude that, in spite of the fact that vibrations of the system machine/tool/workpiece have an adverse effect upon the form of the workpiece on a macro-scale, the cutting process and upon the individual elements of the system, they may result in

Figure 3. Clearance face of the worn tool after the completion of the experiment (b) in Figure 1 (reproduced two-thirds of original size)

lower value for surface finish as measured across the feed marks when concentrated wear is predominant. It may be pointed out that a similar effect has been observed when high frequency vibrations were induced in a grinding operation[9].

Yours faithfully,

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